Electronic Supplementary Information for

Pure *E/Z* isomers of *N*-methylpyrrole-benzohydrazide-based BF_2 complexes: Remarkable aggregation-, crystallization-induced emission switching properties and application in sensing intracellular pH microenvironment

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Contents:

1. Crystal packings and selected parameters

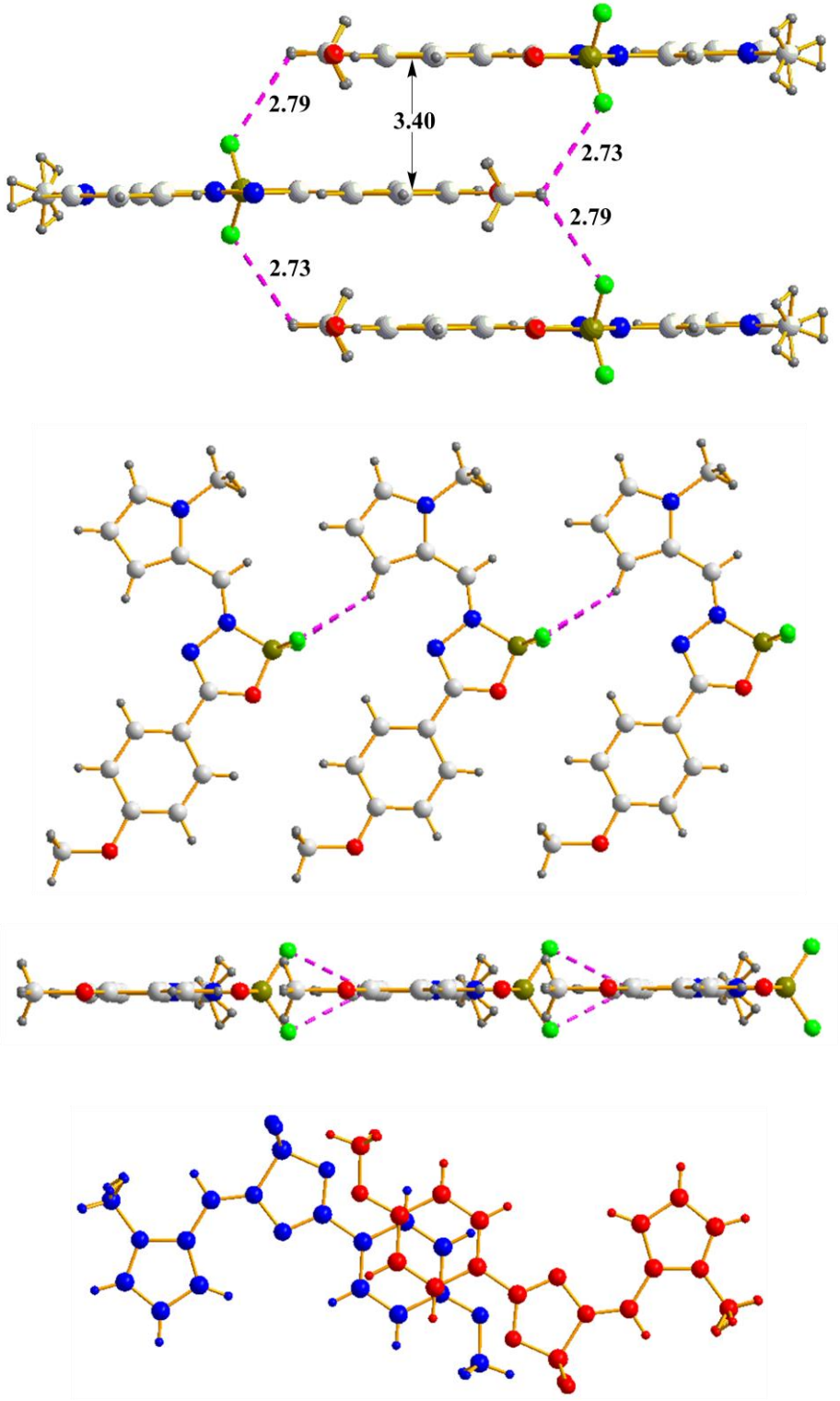


Figure S1. Crystal-packing pattern of **1a** between the adjacent interlayered crystals from side view. Interlayer distance is 3.40 Å. Intermolecular hydrogen bond lengths are 2.79 and 2.73 Å. C, light gray; H, gray; N, blue; O, red; B, dark yellow; F, bight green.

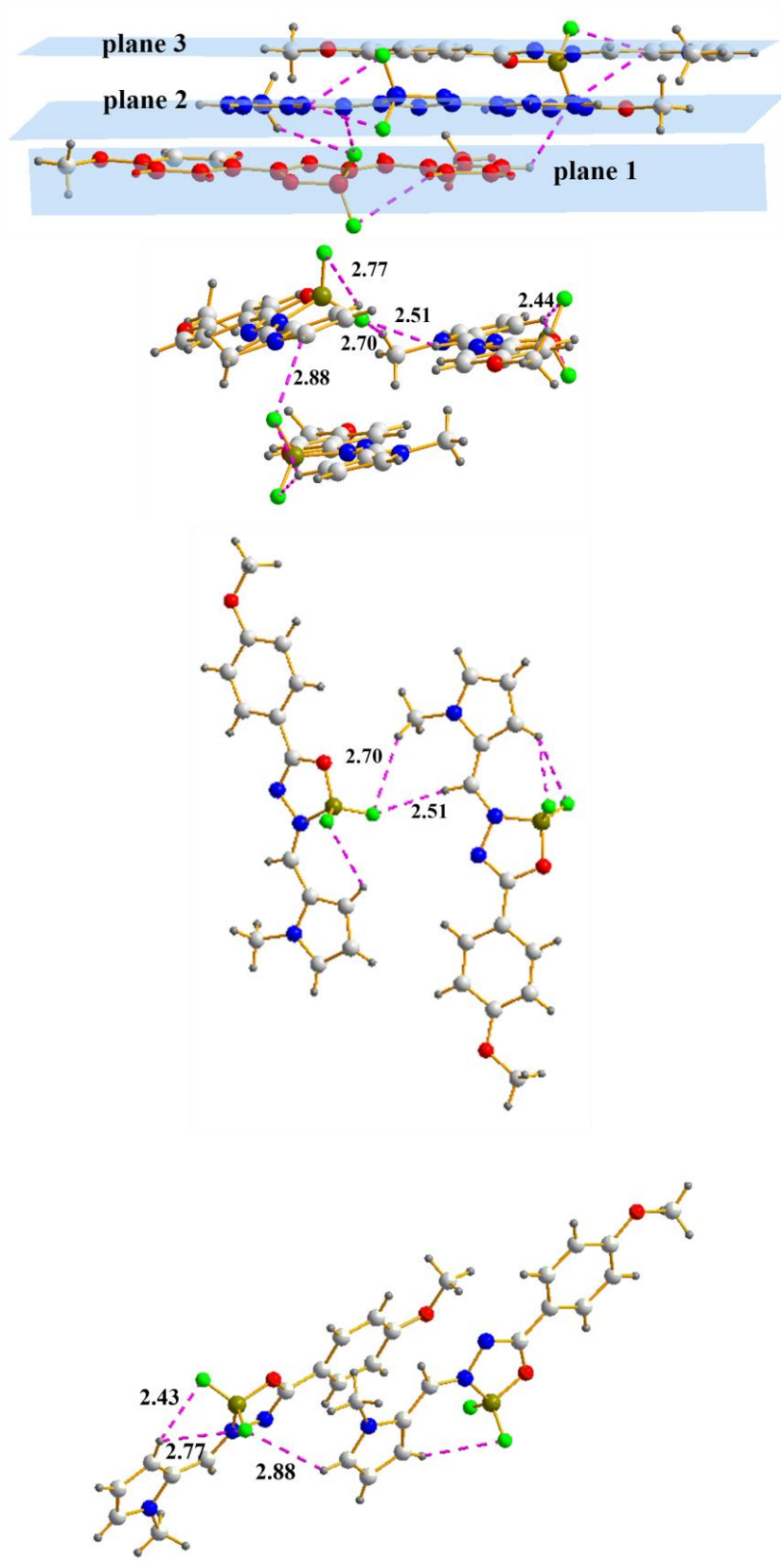


Figure S2. Crystal-packing pattern of **1b** between the adjacent interlayered crystals from side view. Multiple intermolecular hydrogen bond and intramolecular hydrogen bond are given above. C, light gray; H, gray; N, blue; O, red; B, dark yellow; F, bight green.

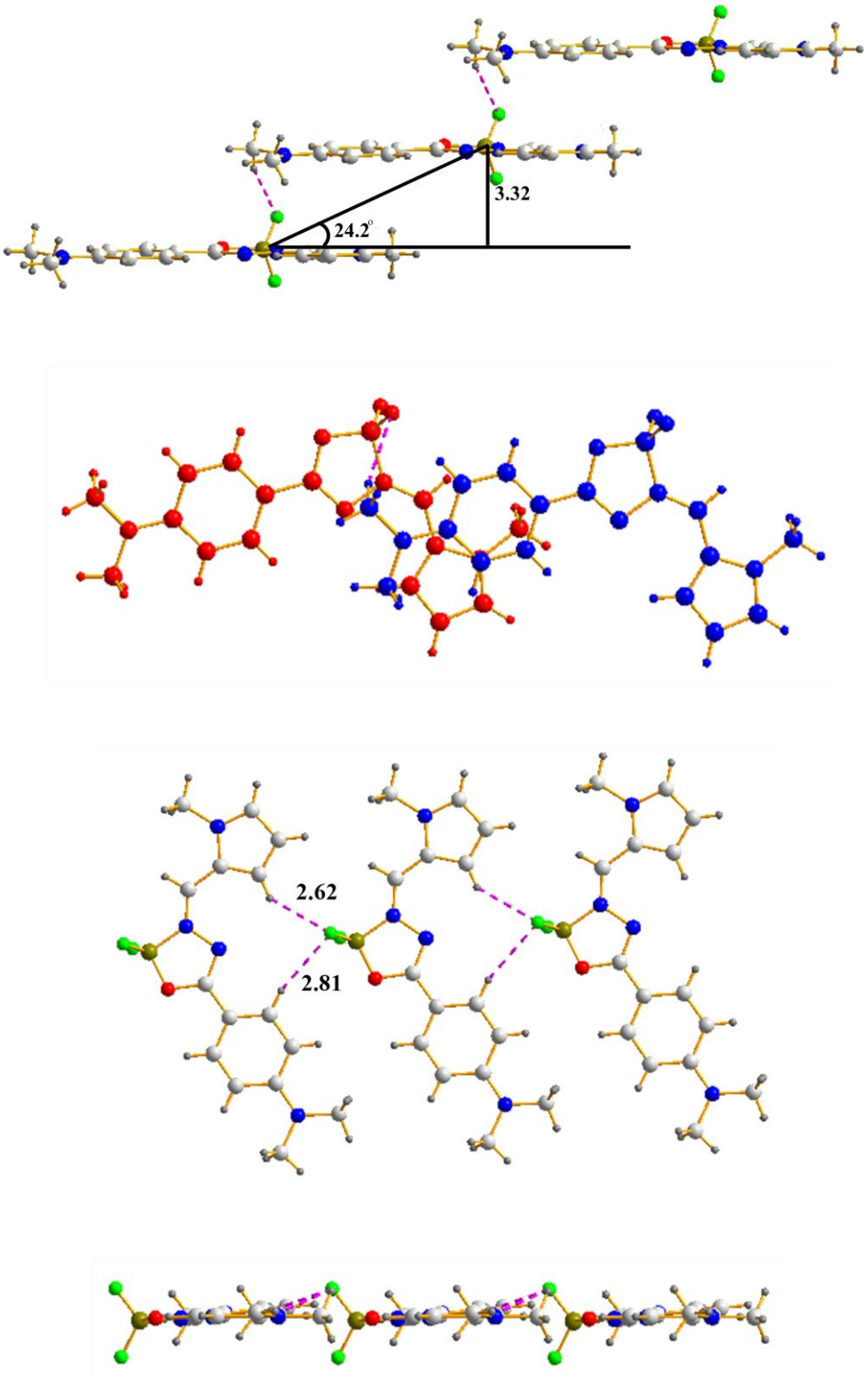


Figure S3. Crystal-packing pattern of **2a** between the adjacent interlayered crystals from side view. Interlayer distance is 3.32 Å. Slip angel of 24.2° for coplanar inclined arrangements of its transition dipole. Intermolecular hydrogen bond lengths are 2.62 and 2.81 Å. C, light gray; H, gray; N, blue; O, red; B, dark yellow; F, bight green.

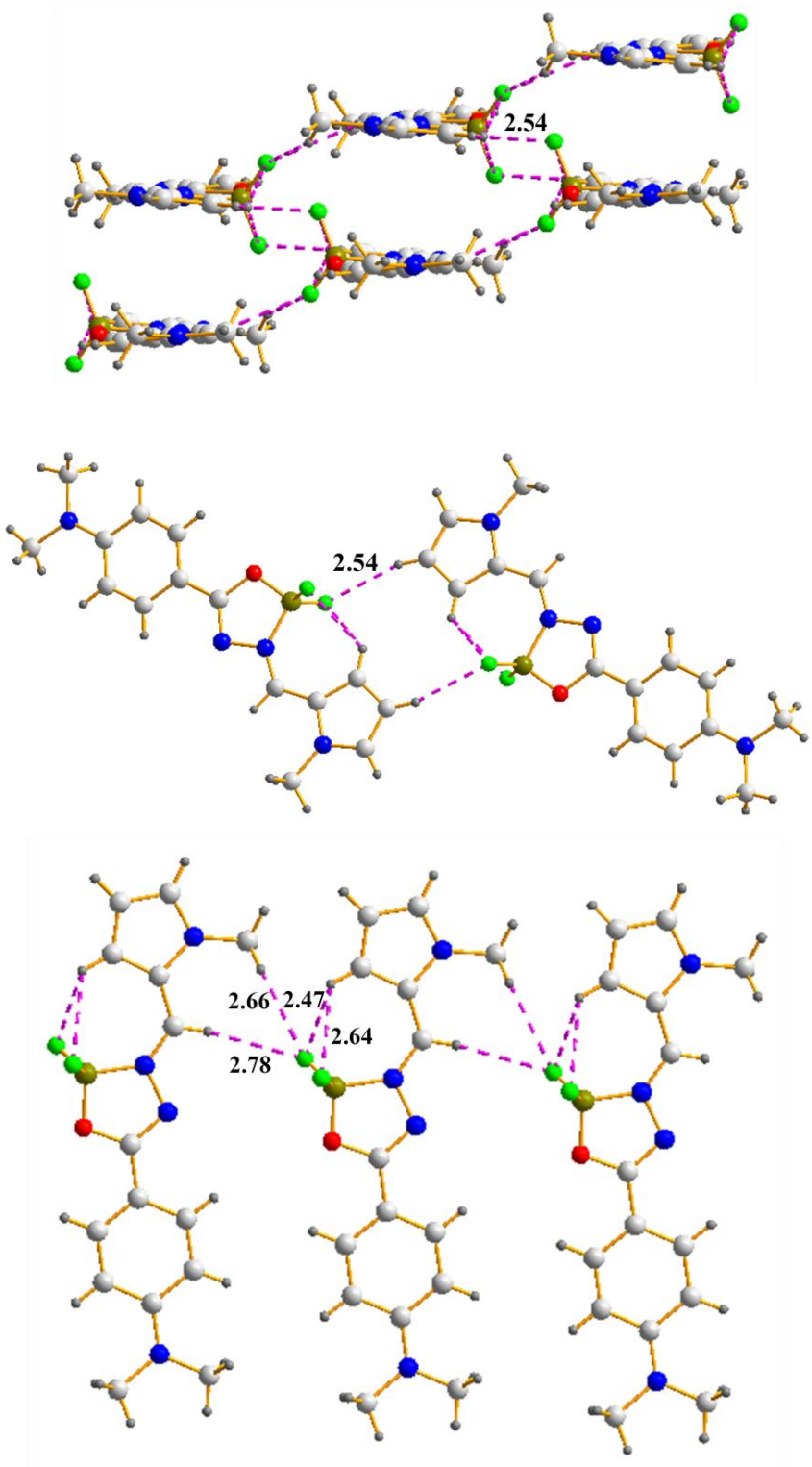


Figure S4. Crystal-packing pattern of **2b** between the adjacent interlayered crystals from side view. Multiple intermolecular hydrogen bond (2.54, 2.66 and 2.78 Å) and intramolecular hydrogen bond (2.47 and 2.64 Å) are given above. C, light gray; H, gray; N, blue; O, red; B, dark yellow; F, bight green.

Table S1. Selected bond lengths [Å] and dihedral angles [deg] of **1a**, **1b**, **2a** and **2b** obtained from crystallography.

dyes	B-N bond distances (Å)	B-O bond distances (Å)	N-N bond distances (Å)	dihedral angles between N-methylp-yrrolic ring and newly formed ring (deg)	dihedral angles of N-methylpyrrolic ring and the aromatic ring (deg)	dihedral angles between the newly formed ring and the aromatic ring (deg)
1a	1.579	1.472	1.397	0.000	0.000	0.000
1b	1.587	1.467	1.407	8.63(2)	3.07(2)	5.58(2)
2a	1.571	1.469	1.404	4.23(2)	5.62(2)	2.40(2)
2b	1.584	1.468	1.408	6.05(2)	10.08(2)	7.39(2)

Table S2. Crystal data and structure refinement for **1a** and **1b**

Identification code	**1a**	**1b**
Empirical formula	$C_{14}H_{14}BF_2N_3O_2$	$C_{14}H_{15}BF_2N_3O_2$
Formula weight	305.09	306.10
Temperature/K	293(2)	273.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/m$	$P2_1/n$
a/Å	7.3108(5)	10.8986(2)
b/Å	6.7983(5)	11.8661(2)
c/Å	14.1226(11)	11.1113(2)
α/°	90	90
β/°	91.598(2)	91.8440(10)
γ/°	90	90
Volume/Å^3	701.63(9)	1436.21(4)
Z	2	4
ρ_{calc} g/cm^3	1.444	1.416
μ/mm^{-1}	0.115	0.956
F(000)	316.0	636.0
Crystal size/mm^3	0.23 × 0.18 × 0.06	0.23 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.206 to 55.024	10.912 to 133.096
Index ranges	$-9 \le h \le 9$, $-8 \le k \le 8$, $-18 \le l \le 18$	$-12 \le h \le 12$, $-14 \le k \le 14$, $-10 \le l \le 13$
Reflections collected	19360	10675
Independent reflections	1744 [R_{int} = 0.0462, R_{sigma} = 0.0232]	2501 [R_{int} = 0.0252, R_{sigma} = 0.0219]
Data/restraints/parameters	1744/0/132	2501/0/201
Goodness-of-fit on F^2	1.055	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0441, wR_2 = 0.1016	R_1 = 0.0395, wR_2 = 0.1089
Final R indexes [all data]	R_1 = 0.0663, wR_2 = 0.1120	R_1 = 0.0439, wR_2 = 0.1133
Largest diff. peak/hole / e Å^{-3}	0.19/-0.27	0.15/-0.50

Table S3. Crystal data and structure refinement for **2a** and **2b**

Identification code	**2a**	**2b**
Empirical formula	$C_{16}H_{17}F_2N_4O$	$C_{15}H_{17}BF_2N_4O$
Formula weight	319.33	318.13
Temperature/K	273.15	293(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	7.2781(12)	6.7077(2)
b/Å	8.5866(14)	8.4933(3)
c/Å	13.586(2)	14.4139(5)
α/°	72.984(6)	91.8700(10)
β/°	80.919(6)	102.8680(10)
γ/°	72.590(6)	107.3170(10)
Volume/$Å^3$	772.4(2)	759.93(4)
Z	2	2
$\rho_{calc}g/cm^3$	1.373	1.390
μ/mm^{-1}	0.106	0.106
F(000)	334.0	332.0
Crystal size/mm^3	0.28 × 0.19 × 0.13	0.23 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.884 to 49.992	5.832 to 49.982
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 10$, $-16 \le l \le 16$	$-7 \le h \le 7$, $-10 \le k \le 10$, $-17 \le l \le 17$
Reflections collected	11719	14692
Independent reflections	2615 [R_{int} = 0.0409, R_{sigma} = 0.0361]	2644 [R_{int} = 0.0602, R_{sigma} = 0.0276]
Data/restraints/parameters	2615/0/211	2644/0/211
Goodness-of-fit on F^2	1.075	1.158
Final R indexes [I>=2σ (I)]	R_1 = 0.0933, wR_2 = 0.2249	R_1 = 0.0422, wR_2 = 0.1204
Final R indexes [all data]	R_1 = 0.1169, wR_2 = 0.2369	R_1 = 0.0509, wR_2 = 0.1344
Largest diff. peak/hole / e $Å^{-3}$	0.35/-0.39	0.33/-0.32

2. Photophysical properties

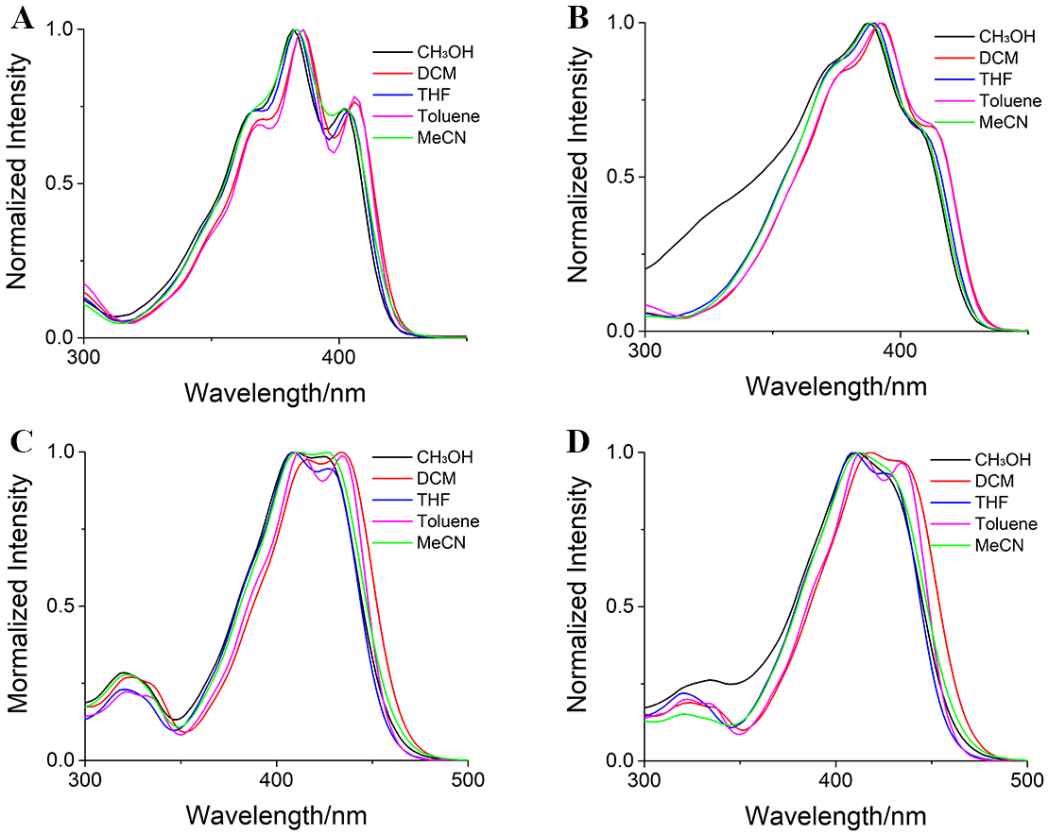


Figure S5. UV-vis spectra of (A) **1a**, (B) **1b**, (C) **2a** and (D) **2b** in different solvents.

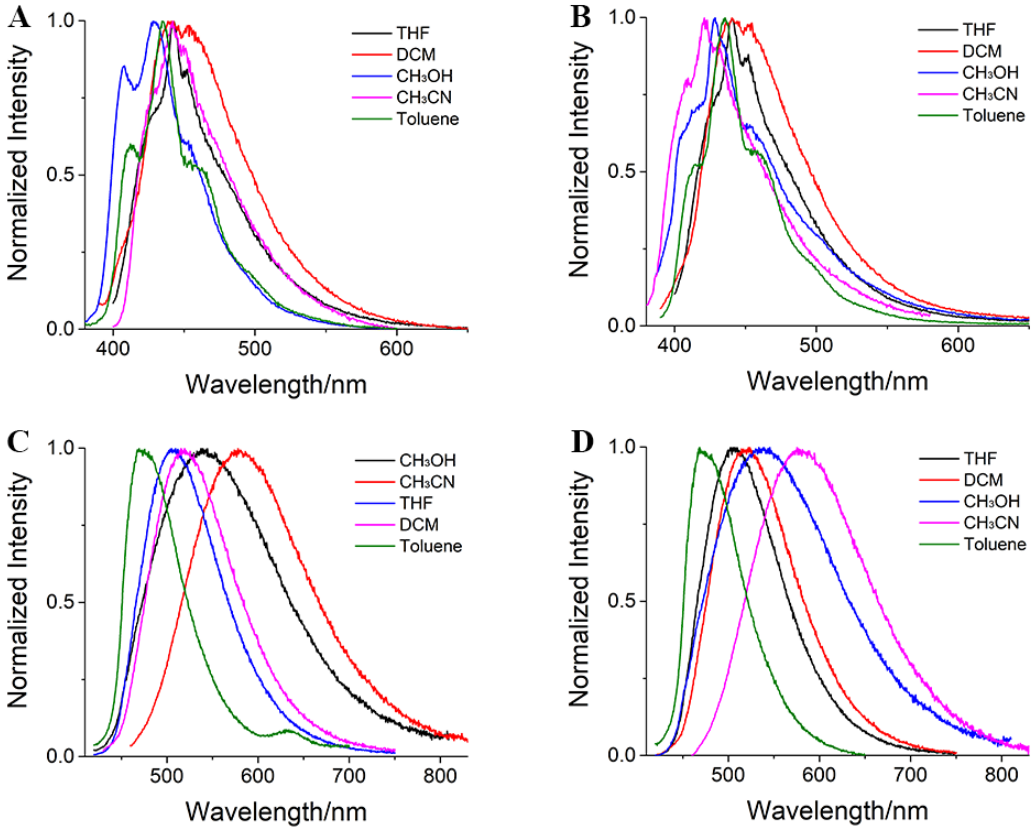


Figure S6. PL spectra of (A) **1a**, (B) **1b**, (C) **2a** and (D) **2b** in different solvents.

Table S4. Photophysical properties in organic solvents and in solid state

dyes	solvents	λ_{abs}^{max} (nm)	λ_{Em}^{max} (nm)	$log\varepsilon^{max}$	ϕ
1a	DCM	386	443	4.52	0.018
	CH_3OH	382	428	4.71	0.050
	Toluene	386	435	4.54	0.016
	THF	384	442	4.54	0.017
	MeCN	384	442	4.76	0.014
	solid state	\	509	\	0.137
1b	DCM	392	442	4.65	0.019
	CH_3OH	388	428	4.65	0.046
	Toluene	390	435	4.59	0.012
	THF	390	442	4.69	0.035
	MeCN	388	441	4.79	0.014
	solid state	\	505	\	0.140
2a	DCM	434	518	4.69	0.064
	CH_3OH	410	539	4.69	0.071
	Toluene	412	467	4.77	0.018
	THF	408	507	4.75	0.067
	MeCN	412	579	4.76	0.029
	solid state	\	552	\	0.108
2b	DCM	418	522	4.61	0.089
	CH_3OH	410	538	4.77	0.193
	Toluene	414	468	4.63	0.049
	THF	410	506	4.64	0.061
	MeCN	412	579	4.81	0.027
	solid state	\	571	\	0.269

3. DFT calculations

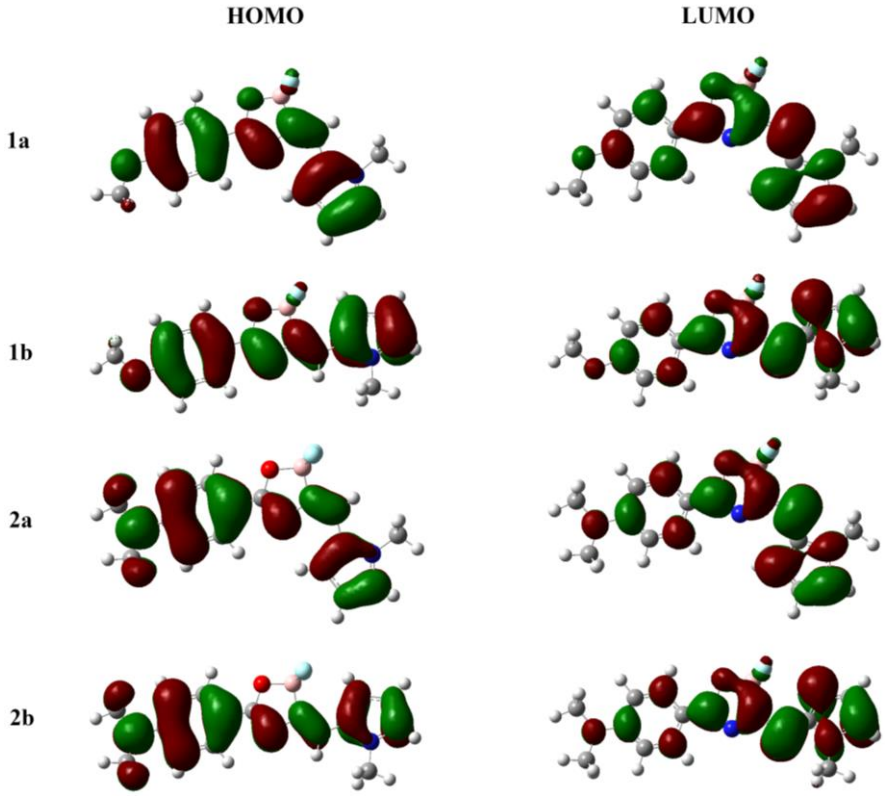


Figure S7. Optimized structures and orbits of **1** and **2** at the B3LYP/6-31G (d, p) level.

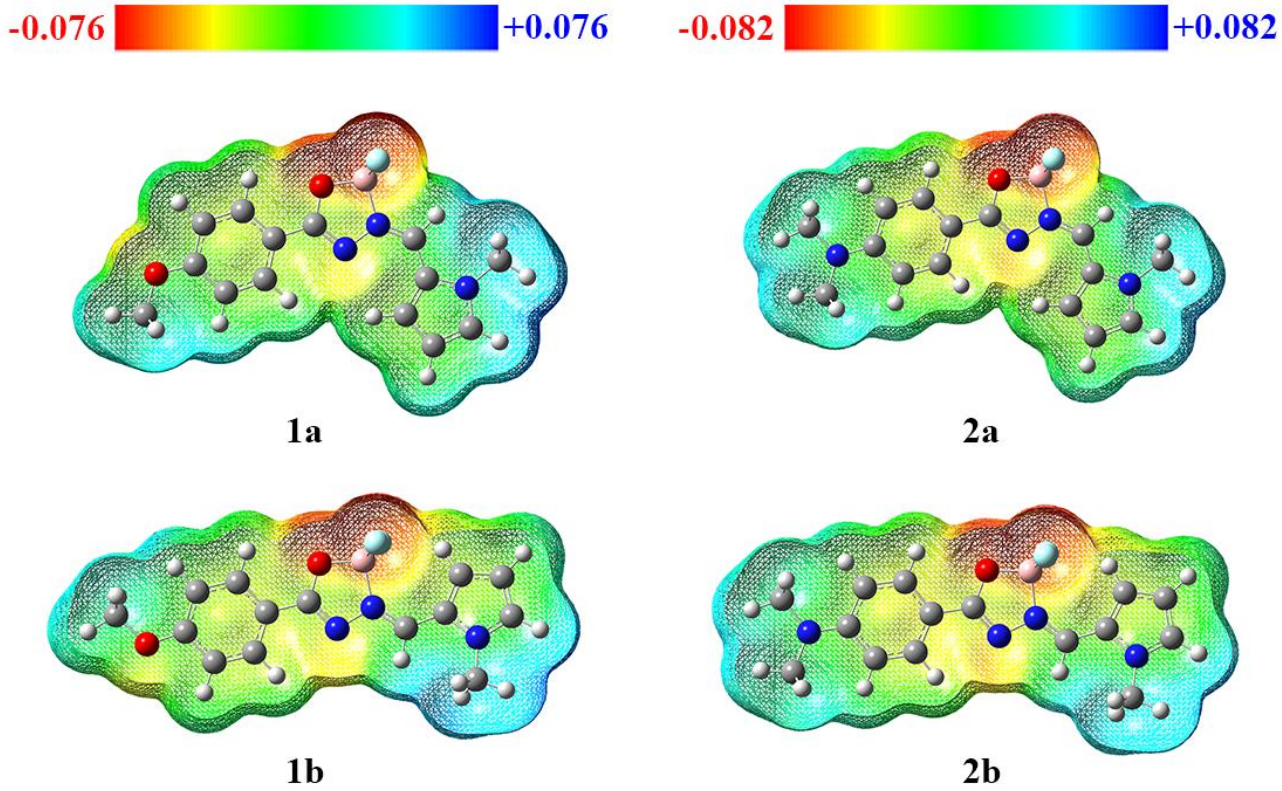


Figure S8. The molecular electrostatic potential in S_0 state.

Table S5. (E)-MPOAB **1a** coordinates.

C	-3.59985	-1.38832	-2.3E-05	N	4.555853	-1.24793	9.33E-06
C	-4.64615	-0.45095	-1E-05	C	5.667953	-0.30303	-0.00016
C	-4.35173	0.923944	1.95E-05	O	-5.96422	-0.77064	-2.9E-05
C	-3.03565	1.353926	3.81E-05	C	-6.33435	-2.14991	-6.9E-05
C	-1.97834	0.424323	3.53E-05	H	-3.80404	-2.45167	-4.8E-05
C	-2.2816	-0.94585	-3.8E-06	H	-5.17393	1.631517	2.8E-05
C	-0.59511	0.889934	6.28E-05	H	-2.80998	2.414011	6.24E-05
N	0.43288	0.06719	0.000051	H	-1.47351	-1.66883	-1.5E-05
N	1.548307	0.888191	1.76E-05	H	3.525365	1.200431	-4.3E-05
O	-0.36036	2.196162	-3.1E-05	H	1.410554	-2.21868	0.000133
C	2.769024	0.421621	6.08E-06	H	3.224533	-4.24649	5.3E-05
B	1.111908	2.420724	-7.7E-06	H	5.667361	-3.05275	1.73E-05
F	1.541687	3.062478	-1.14246	H	6.600007	-0.86732	0.000252
F	1.541628	3.062491	1.14247	H	5.641967	0.327968	-0.89213
C	3.193128	-0.9299	3.89E-05	H	5.641628	0.328645	0.891318
C	2.485686	-2.14619	8.45E-05	H	-7.42411	-2.16494	-8.5E-05
C	3.424046	-3.18476	3.94E-05	H	-5.96302	-2.66182	-0.89461
C	4.687647	-2.59701	2.98E-05	H	-5.96304	-2.66187	0.894452

Table S6. (Z)-MPOAB **1b** coordinates.

C	-4.08563	1.644598	0.142539	N	4.791146	1.251367	-0.05135
C	-5.01126	0.588357	0.042428	C	4.681133	2.686606	-0.29148
C	-4.55176	-0.73172	-0.0695	O	-6.31878	0.950899	0.063266
C	-3.18173	-0.98409	-0.07992	C	-7.31278	-0.06957	-0.03373
C	-2.25373	0.061034	0.019242	H	-4.46226	2.658313	0.228454
C	-2.72765	1.383495	0.131166	H	-5.24535	-1.55933	-0.14903
C	-0.82129	-0.22187	0.004946	H	-2.82444	-2.0039	-0.16709
N	0.085419	0.722116	0.075473	H	-2.01595	2.197775	0.209087
N	1.314534	0.064562	0.043313	H	2.206672	1.875664	0.064237
O	-0.41406	-1.48492	-0.08256	H	3.739471	-1.82615	0.475656
C	2.392035	0.804463	0.065796	H	6.432662	-1.55776	0.365143
C	3.733724	0.347723	0.096415	H	6.904069	1.086348	-0.06995
B	1.06922	-1.515	-0.10584	H	5.686225	3.102385	-0.35483
F	1.562539	-1.97478	-1.30736	H	4.158102	2.885826	-1.23003
F	1.582642	-2.21983	0.967346	H	4.153097	3.177866	0.529663
C	4.301358	-0.9251	0.287429	H	-8.27243	0.445827	0.003168
C	5.692005	-0.78064	0.245013	H	-7.23016	-0.61783	-0.97865
C	5.96017	0.570118	0.030046	H	-7.24503	-0.77312	0.803405

Table S7. (E)-MPOAB **2a** coordinates.

C	3.247144	-1.38395	-0.00109	C	6.720474	0.079662	0.002251
C	4.328414	-0.45964	-0.00112	C	5.937582	-2.31196	0.000581
C	4.004745	0.923814	-0.0004	H	3.441163	-2.44878	-0.00111
C	2.686989	1.346621	-0.00021	H	4.790845	1.667915	3.04E-06
C	1.62271	0.426607	-0.00051	H	2.466369	2.408307	0.000251
C	1.935881	-0.94643	-0.00088	H	1.130789	-1.67333	-0.00092
C	0.247318	0.889641	-0.00025	H	-3.87565	1.205961	-5.8E-05
N	-0.78614	0.067141	-0.00023	H	-1.76445	-2.21465	0.000641
N	-1.89869	0.887815	-0.00015	H	-3.57921	-4.24391	0.000946
O	0.007685	2.197843	7.57E-06	H	-6.02198	-3.04961	0.000161
C	-3.12102	0.425723	-5.3E-05	H	-5.99373	0.332495	0.891404
B	-1.46147	2.419679	0.00015	H	-5.99353	0.332586	-0.89169
F	-1.89477	3.062594	-1.14196	H	-6.95254	-0.86263	-0.00035
C	-3.54649	-0.92714	5.14E-05	H	7.67048	-0.45321	0.000473
C	-2.83961	-2.14275	0.000502	H	6.692229	0.726193	-0.88372
C	-3.77904	-3.18216	0.000675	H	6.691696	0.719918	0.892853
C	-5.04176	-2.59497	0.00029	H	7.018849	-2.4433	-0.00244
N	-4.90874	-1.24462	-0.00011	H	5.537234	-2.81254	0.891154
C	-6.01985	-0.29924	-0.00017	H	5.53224	-2.81602	-0.88562
N	5.630659	-0.88753	-0.00196	F	-1.89472	3.061958	1.142674

Table S8. (Z)-MPOAB **2b** coordinates.

C	-3.81657	1.368086	0.107518	C	-6.98437	-0.66613	-0.0772
C	-4.72139	0.274132	0.02257	H	-4.19157	2.380917	0.179649
C	-4.16296	-1.02818	-0.07332	H	-4.80793	-1.8947	-0.14179
C	-2.79122	-1.21717	-0.08091	H	-2.39103	-2.22238	-0.15509
C	-1.90315	-0.13055	0.005029	H	-1.78048	2.015582	0.165704
C	-2.449	1.163789	0.099091	H	2.473648	1.884503	0.051339
C	-0.466	-0.34448	-0.00384	H	4.161685	-1.74259	0.515886
N	0.4022	0.640181	0.064668	H	6.842476	-1.36184	0.406103
N	1.657519	0.038299	0.040291	H	7.202057	1.292158	-0.07083
O	0.002553	-1.58919	-0.08322	H	5.898002	3.247754	-0.40255
C	2.703321	0.821935	0.061391	H	4.371546	2.953977	-1.25748
C	4.064853	0.421516	0.101491	H	4.371868	3.275751	0.496683
B	1.482674	-1.55137	-0.09927	H	-8.01249	-0.30684	-0.05423
F	2.004727	-1.99683	-1.29516	H	-6.83654	-1.21438	-1.01629
F	2.023787	-2.22566	0.981579	H	-6.85325	-1.37149	0.752945
C	4.685383	-0.8217	0.314279	C	-6.62716	1.81654	0.123415
C	6.070013	-0.61861	0.272065	H	-7.71492	1.758983	0.130307
C	6.281102	0.737513	0.035802	H	-6.30935	2.322057	1.043704
N	5.082732	1.36677	-0.05908	H	-6.32529	2.438606	-0.72899
C	4.911668	2.791839	-0.32142	N	-6.07902	0.469837	0.033198

4. Supporting Figures

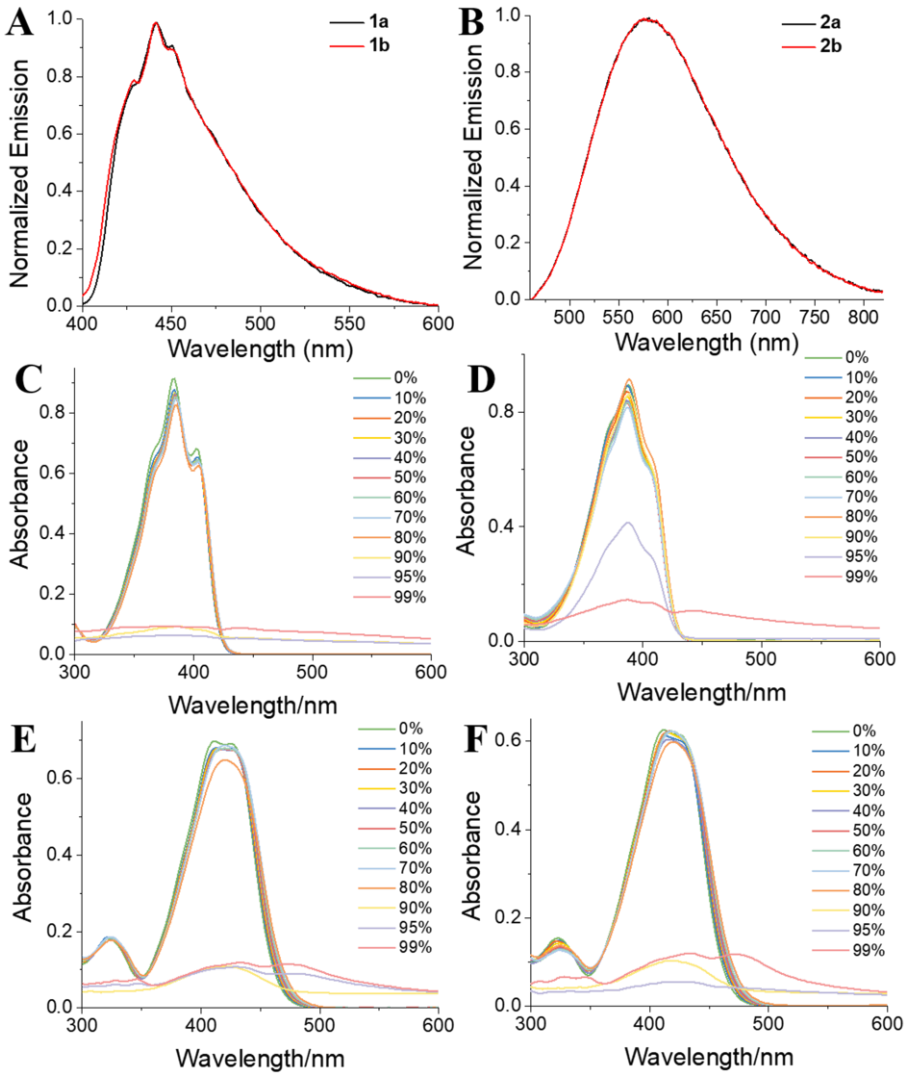


Figure S9. PL spectra of **1a**, **1b** (A) and **2a**, **2b** (B) in acetonitrile; Absorbance spectra of **1a** (1.8×10^{-5} mol/L, C), **1b** (1.7×10^{-5} mol/L, D), **2a** (1.4×10^{-5} mol/L, E) and **2b** (1.4×10^{-5} mol/L, F) in acetonitrile/water with different water fractions (f_w).

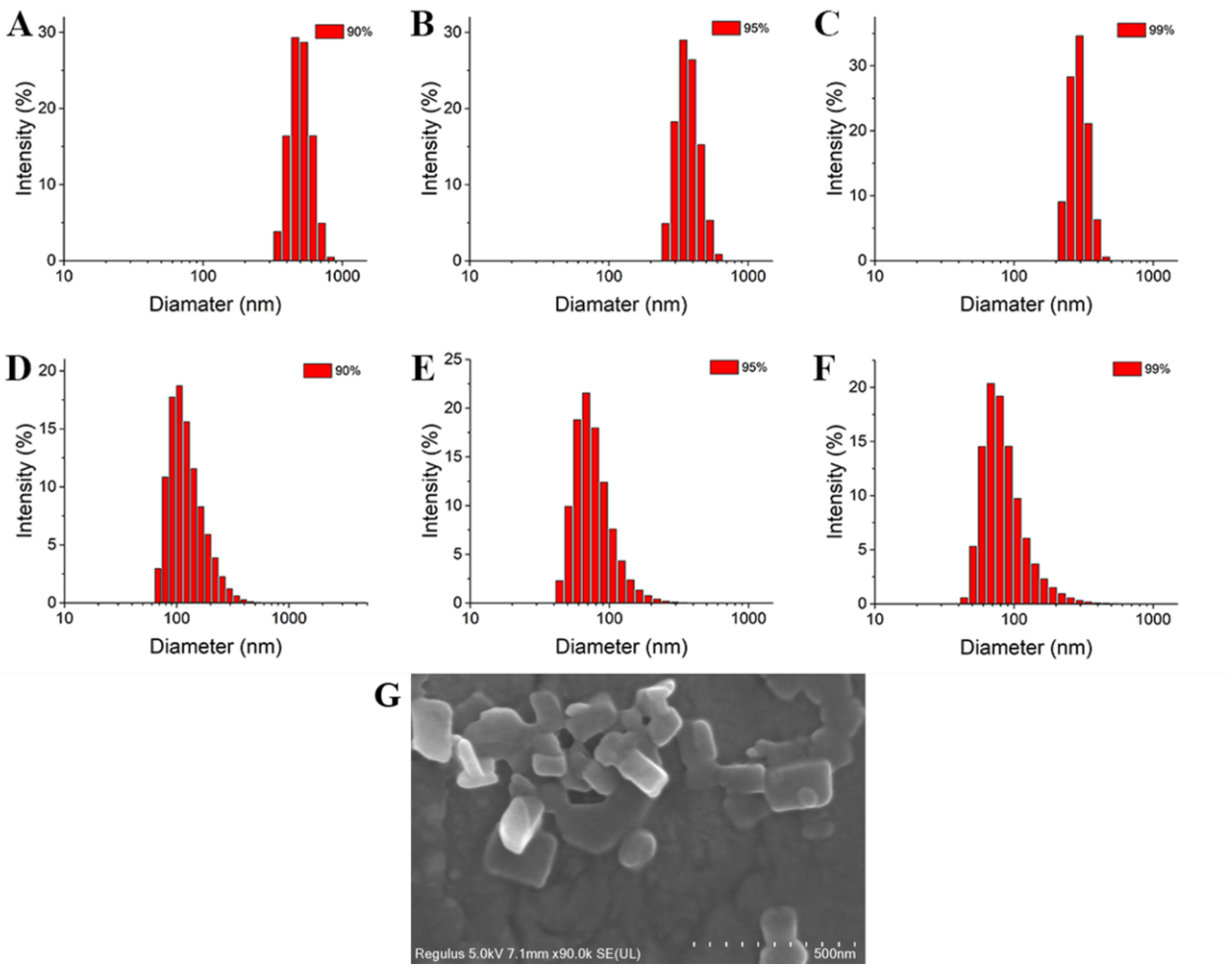
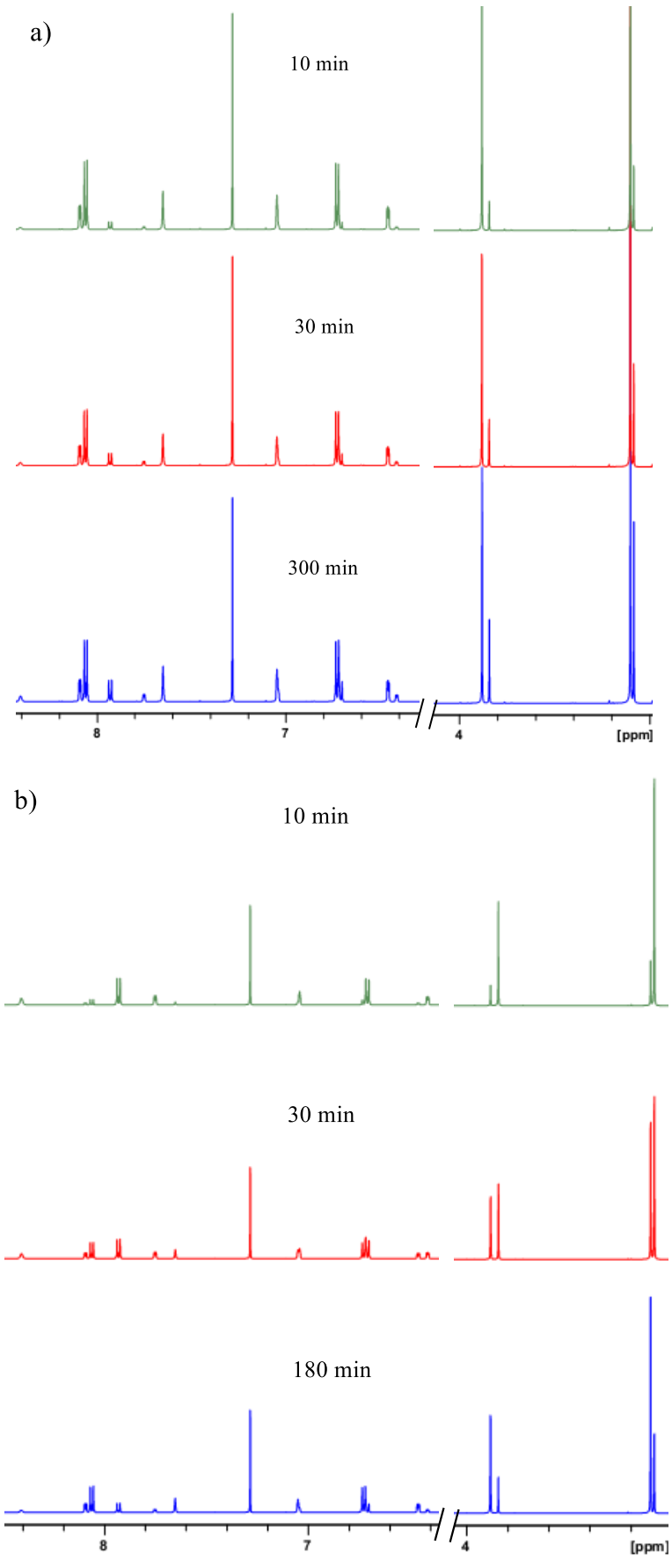


Figure S10. Particle size distributions of **2a** (A, B and C) and **2b** (D, E and F) in acetonitrile/water mixtures with f_w = 90% (A and D), 95% (B and E) and 99% (C and F). The concentration of samples is 15 μM. Average diameter (nm) = A) 505, B) 373, C) 294, D) 129, E) 79, F) 89 and G) SEM of **2b** in acetonitrile/water mixtures with f_w = 99%.


a)
10 min
30 min
300 min
8
7
4
[ppm]
b)
10 min
30 min
180 min
8
7
4
[ppm]

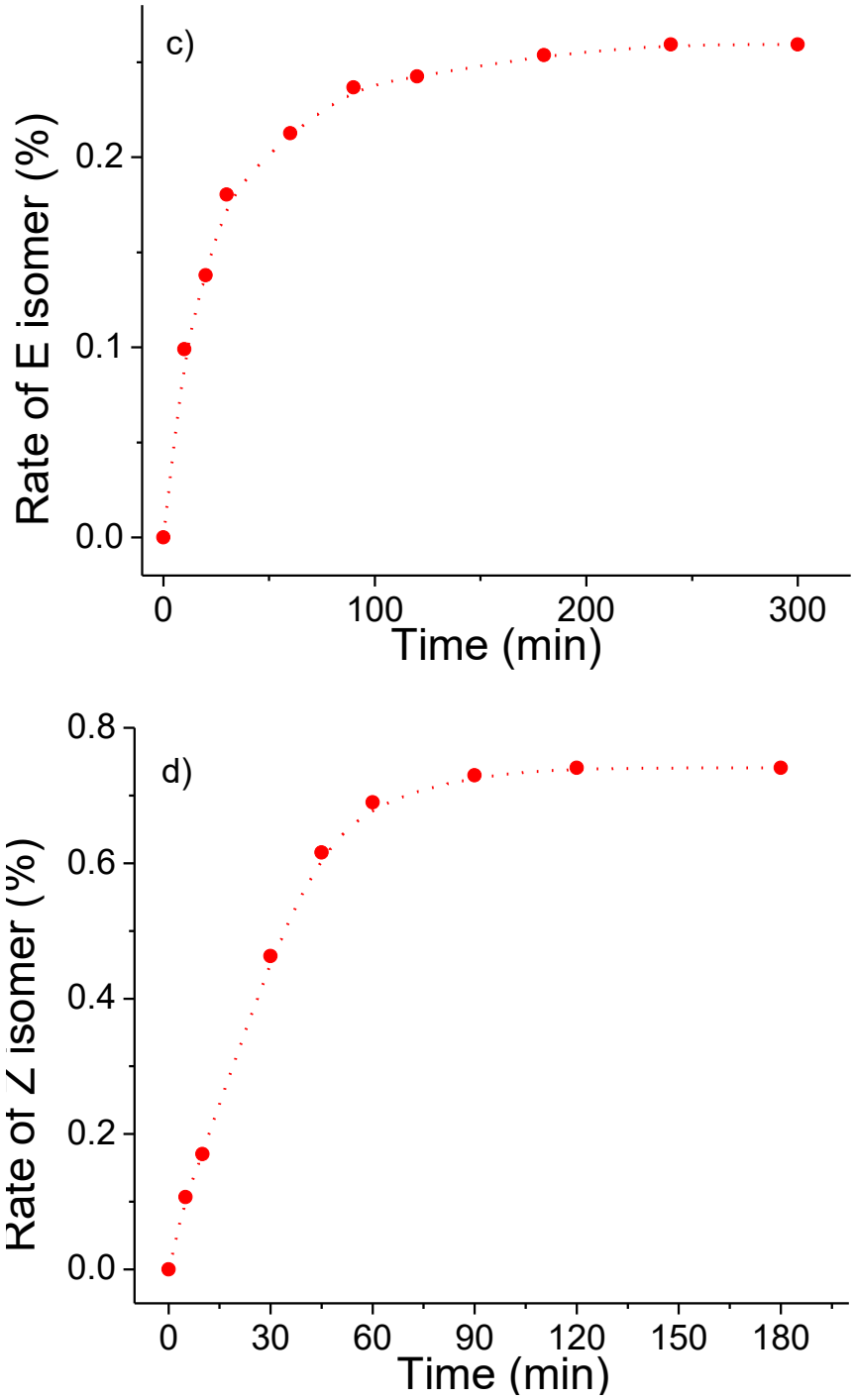


Figure S11. ^{1}H NMR spectra of **2a** (a) and **2b** (b) irradiated for 10 min, 30 min and 300 min in $CDCl_3$. Variations in the amount of E isomer **2b** (c) by irradiating **2a** and Z isomer **2a** (c) by irradiating **2b** with a 18 W white light LED.

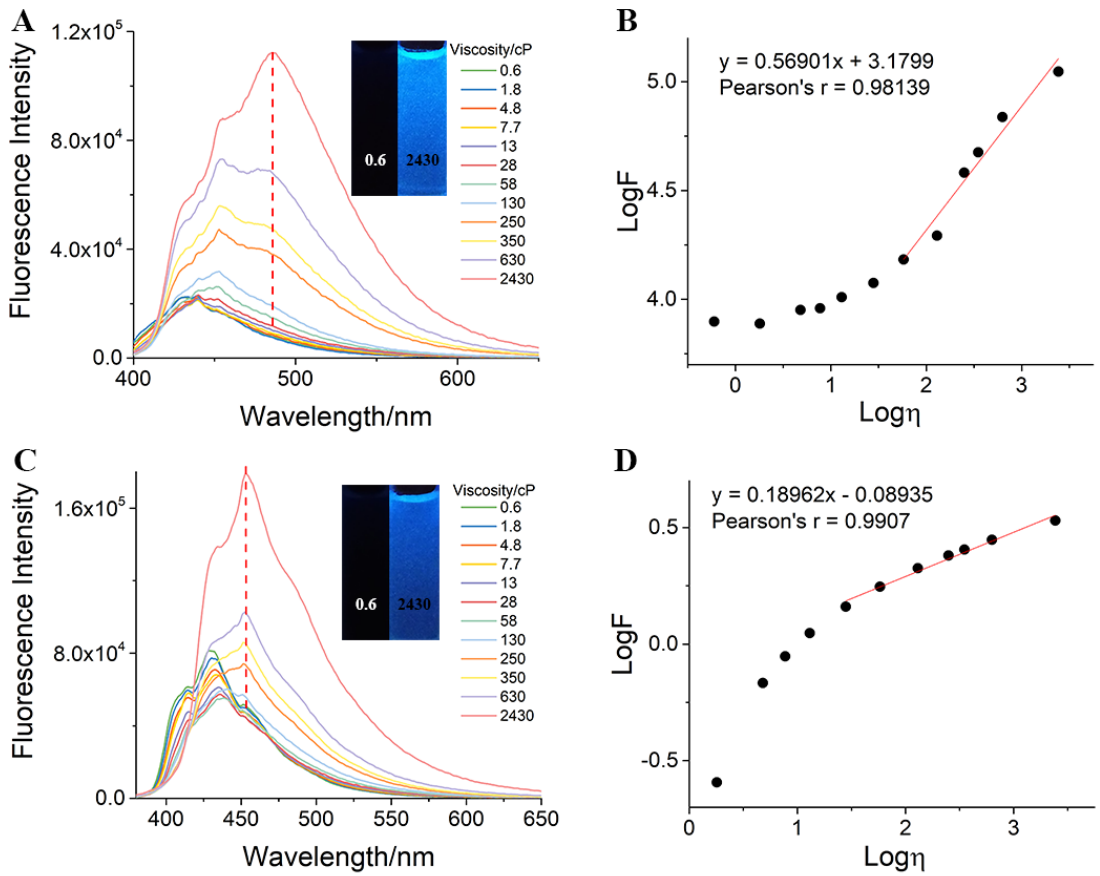


Figure S12. (A) PL spectra of **1a** in CH_3OH/ glycerol solutions with different viscosity. The concentration of **1a** is 2.47×10^{-5} mol/L in each solution. λ_{ex} = 390 nm. (B) **1a** working curve of $\log_{10}(\eta)$ (the logarithm of viscosity value) vs. $\log_{10}(F)$ (the logarithm of fluorescence intensity). (C) PL spectra of **1b** in CH_3OH/glycerol solutions with different viscosity. The concentration of **1b** is 1.44×10^{-5} mol/L in each solution. λ_{ex} = 370 nm. (D) **1b** working curve of $\log_{10}(\eta)$ vs. $\log_{10}(F)$.

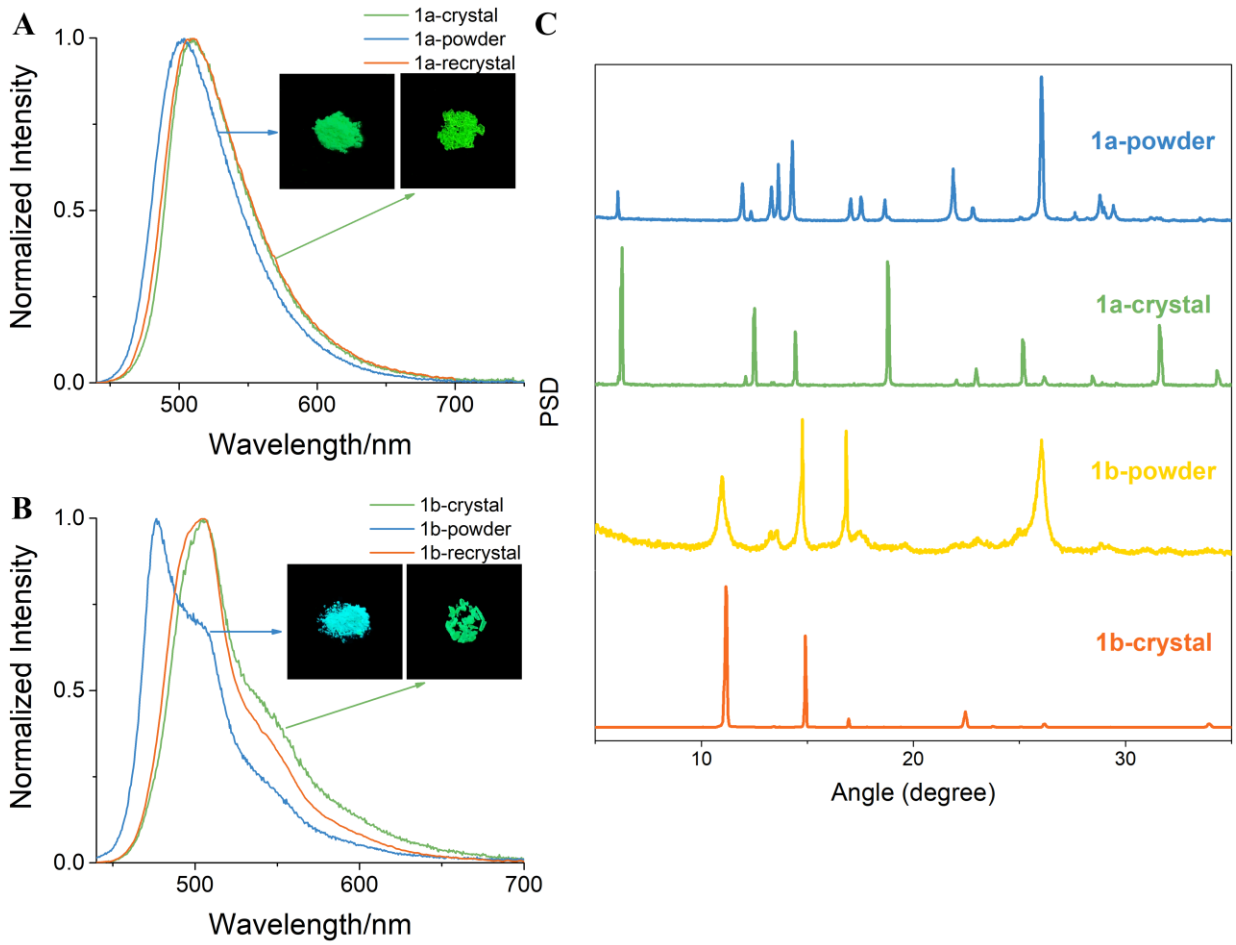


Figure S13. (A) The comparison of the PL spectra between **1a**-powder, **1a**-crystal and **1a**-recrystal. (B) The comparison of the PL spectra between **1b**-powder, **1b**-crystal and **1b**-recrystal. (C) XRD patterns of **1a** and **1b** in powder and crystal states. All powder samples were prepared by grinding the corresponding crystal in the agate mortar for 1 min.

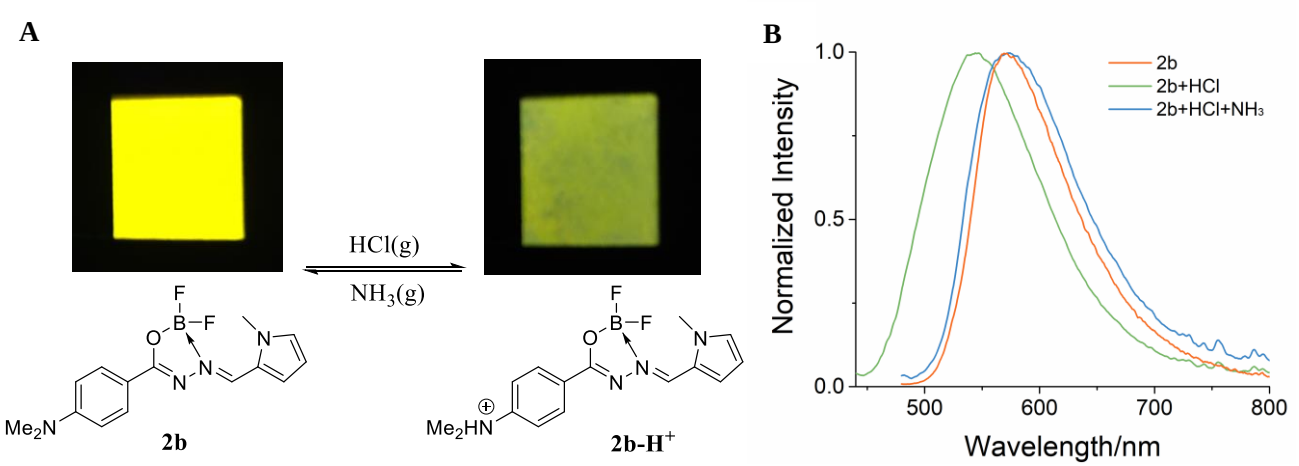


Figure S14. (A) Diagrammatic sketch of acid-base fluorescence response of **2b**. (B) The PL spectra comparison of **2b**, **2b**+HCl and **2b**+HCl+NH_3. The sample solution was dropped upon silex glass and dried to obtain the sample solid film. Every silex glass with sample just be exposed to the HCl or NH_3 vapors about 20 s.

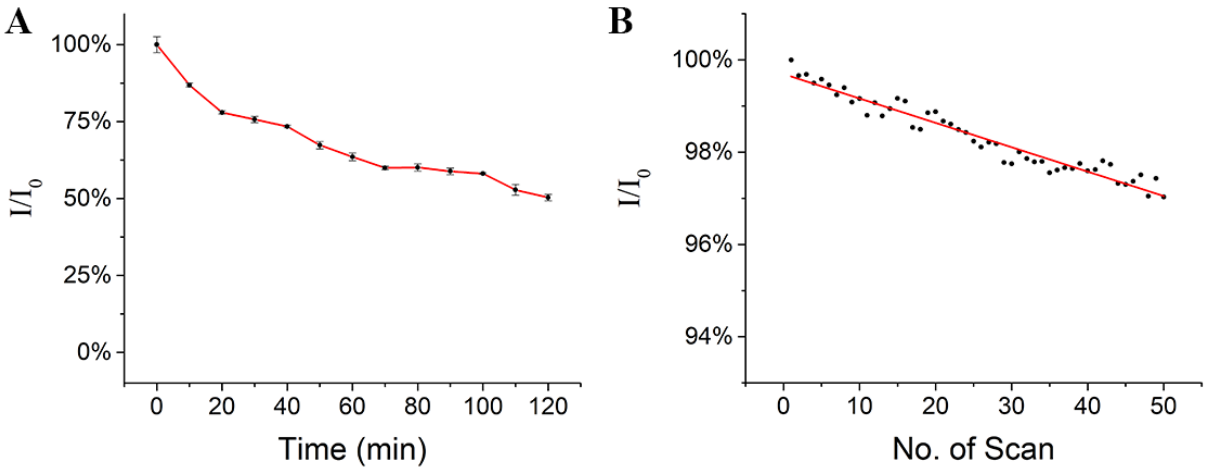
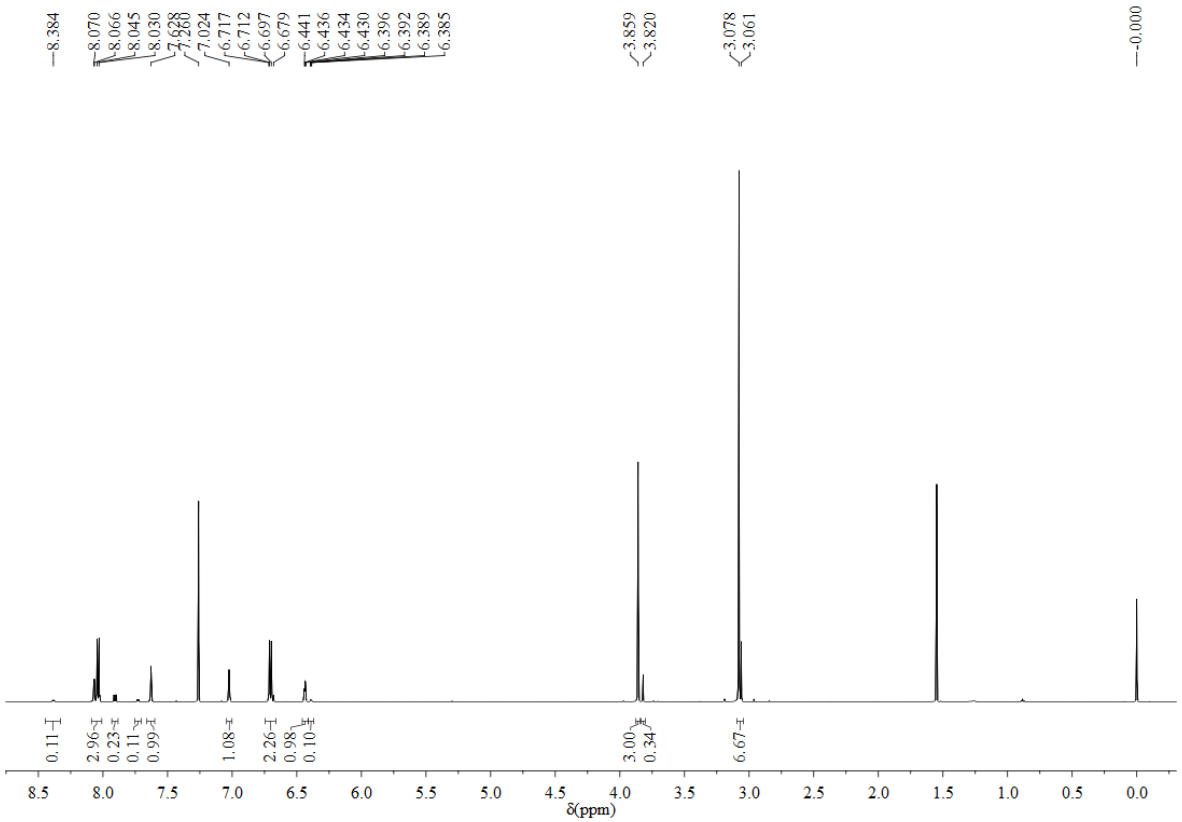
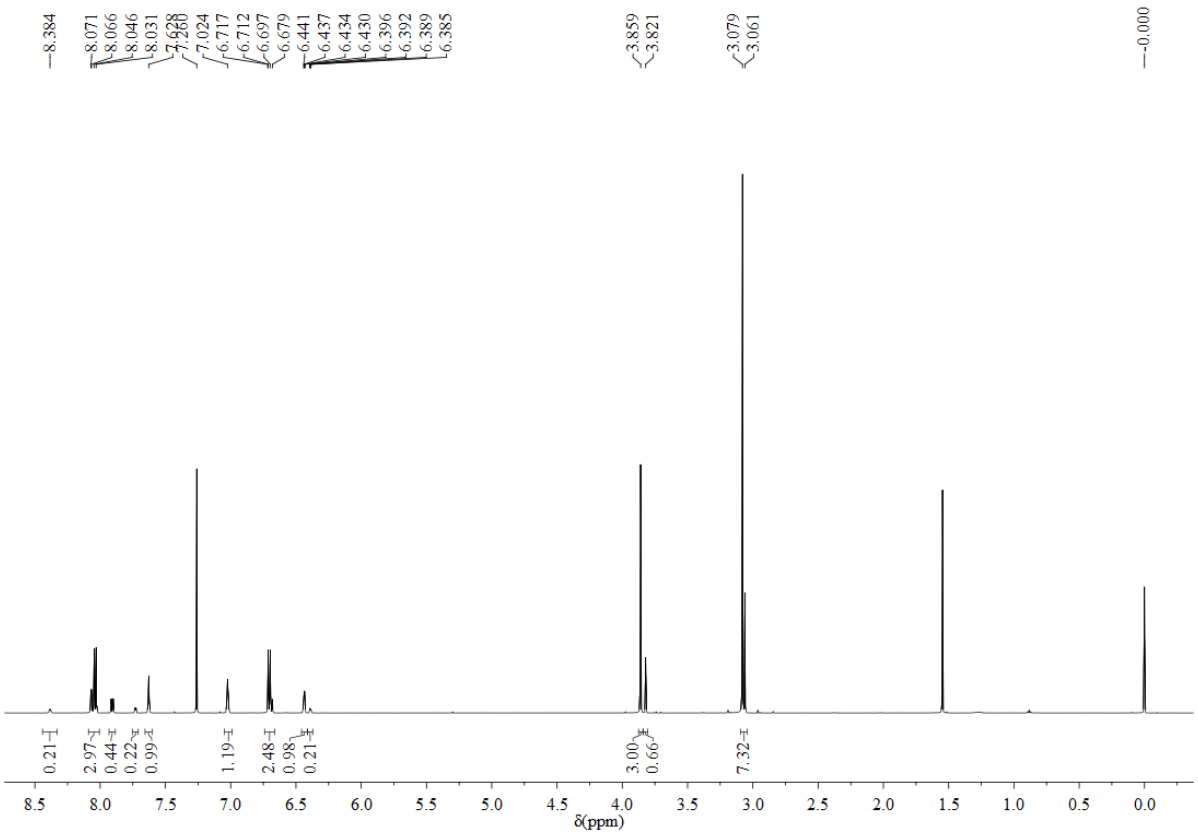


Figure S15. (A) Loss in fluorescence of **2a** NPs in acetonitrile/water mixtures (f_w = 90%) with 2 h Green LED light irradiation. **2a** concentration is 15 μM. The LED light's rated power is 18 W with 490 nm-530 nm green light. The average power density is about 900 mW/cm^2. And the data is shown as the mean value plus a standard deviation (±SD). (B) Loss in fluorescence of MCF-7 cells stained with **2a** NPs with increasing the number of scans of laser irradiation. Concentration: 15 μM; λ_{ex}: 488 nm; scanning rate: 10 s frame^{-1}.

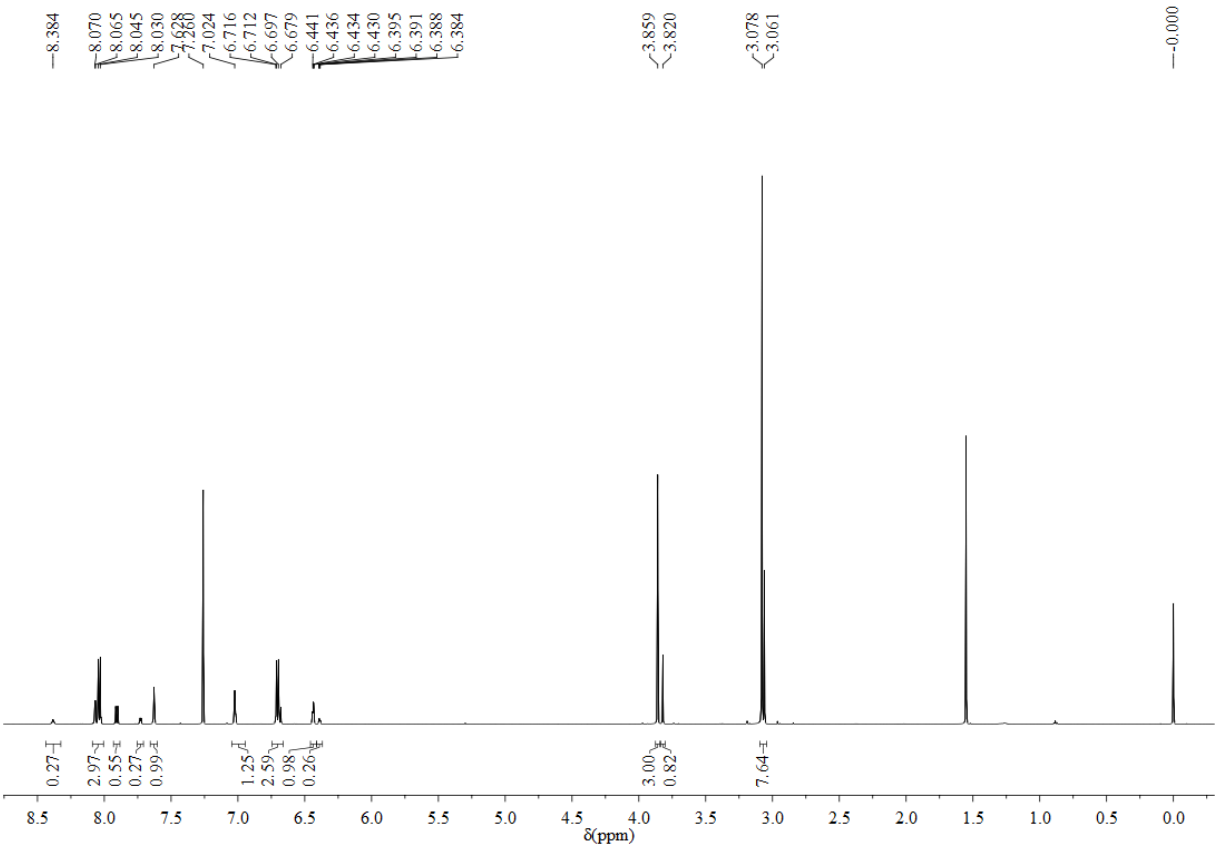
5. Photodynamic isomerization studies by ^{1}H NMR spectra



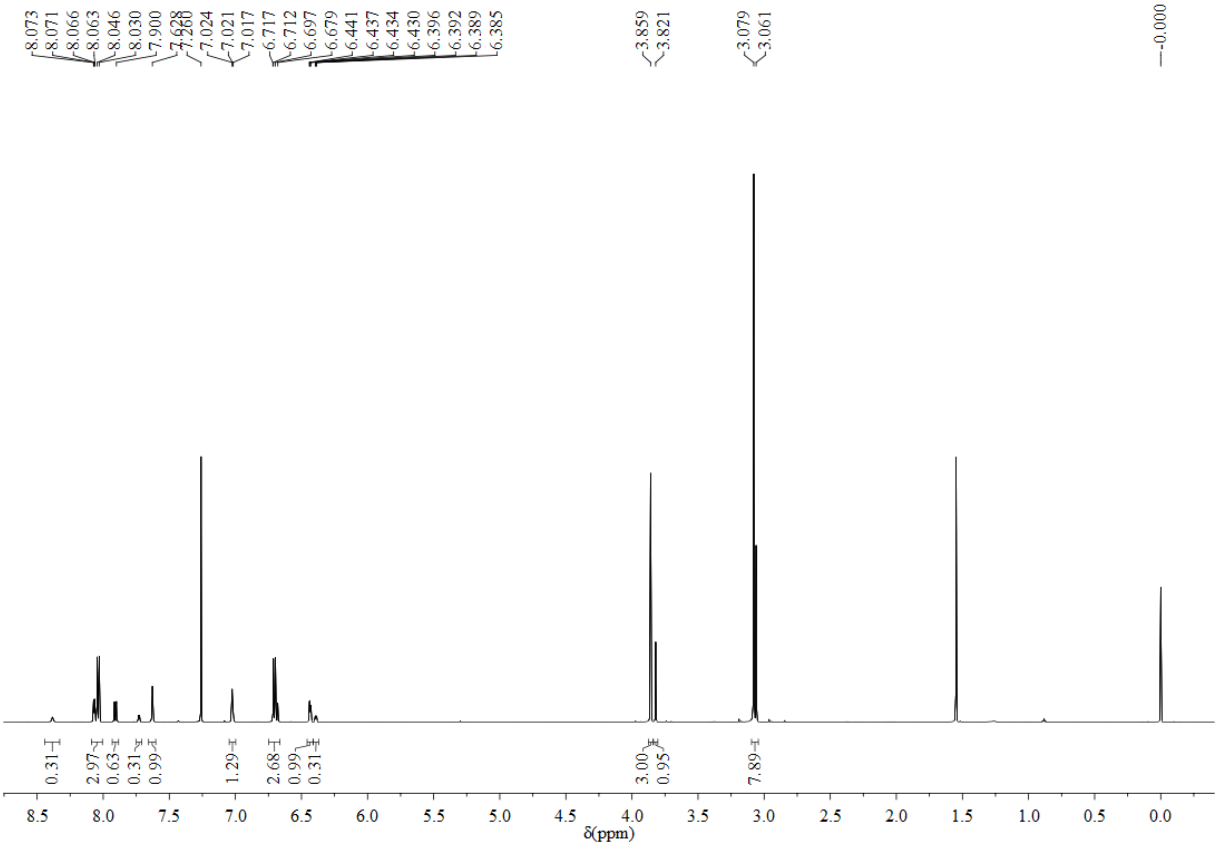
^{1}H NMR spectrum of **2a** which was irradiated by 18W white light LED for 10 min in $CDCl_3$.



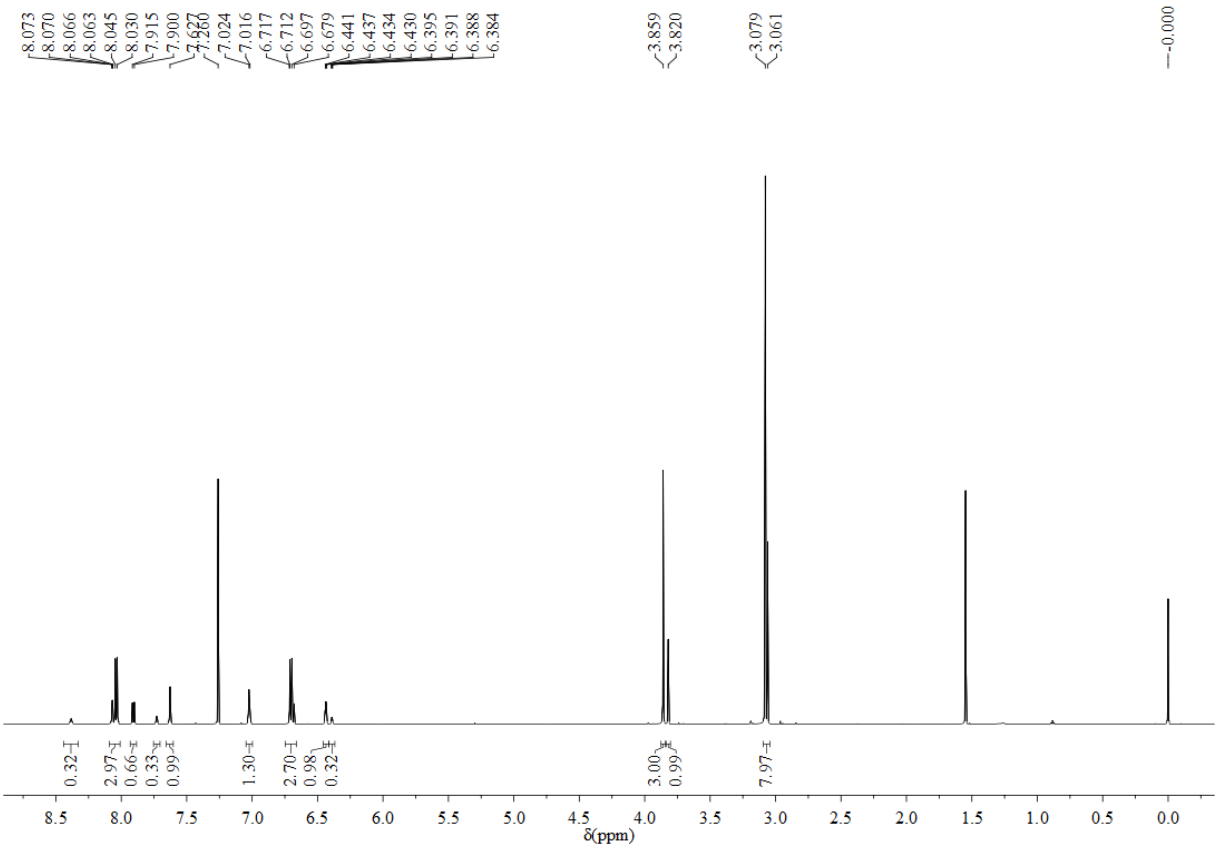
^{1}H NMR spectrum of **2a** which was irradiated by 18W white light LED for 30 min in $CDCl_3$.



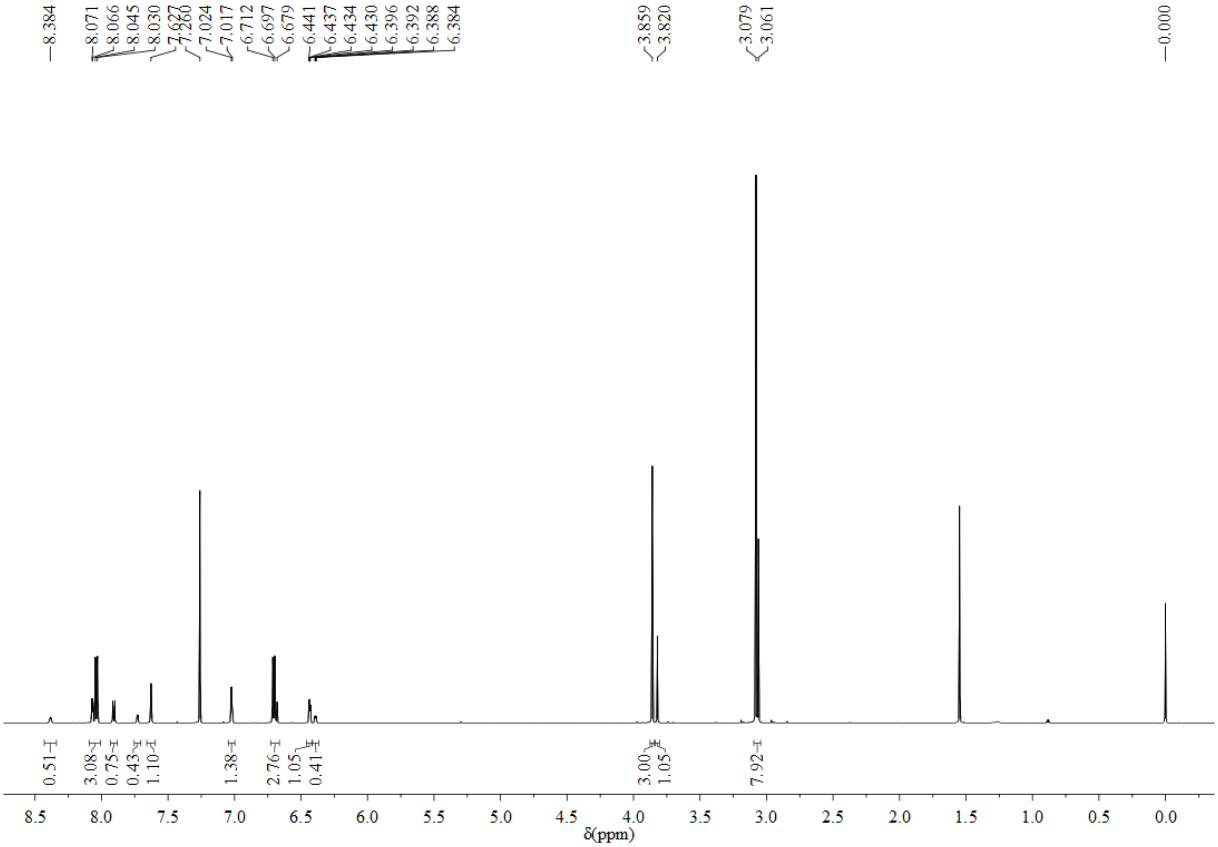
^{1}H NMR spectrum of **2a** which was irradiated by 18W white light LED for 60 min in $CDCl_3$.



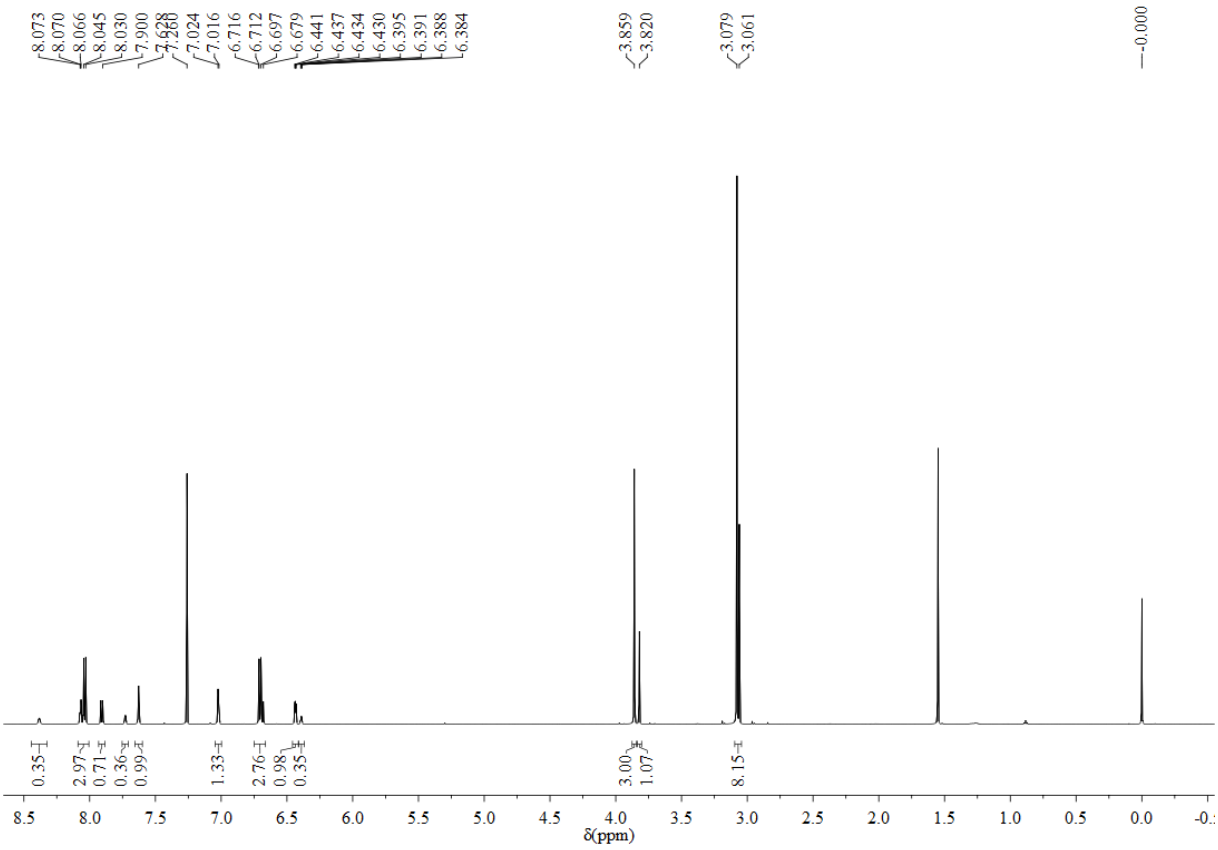
^{1}H NMR spectrum of **2a** which was irradiated by 18W white light LED for 90 min in $CDCl_3$.



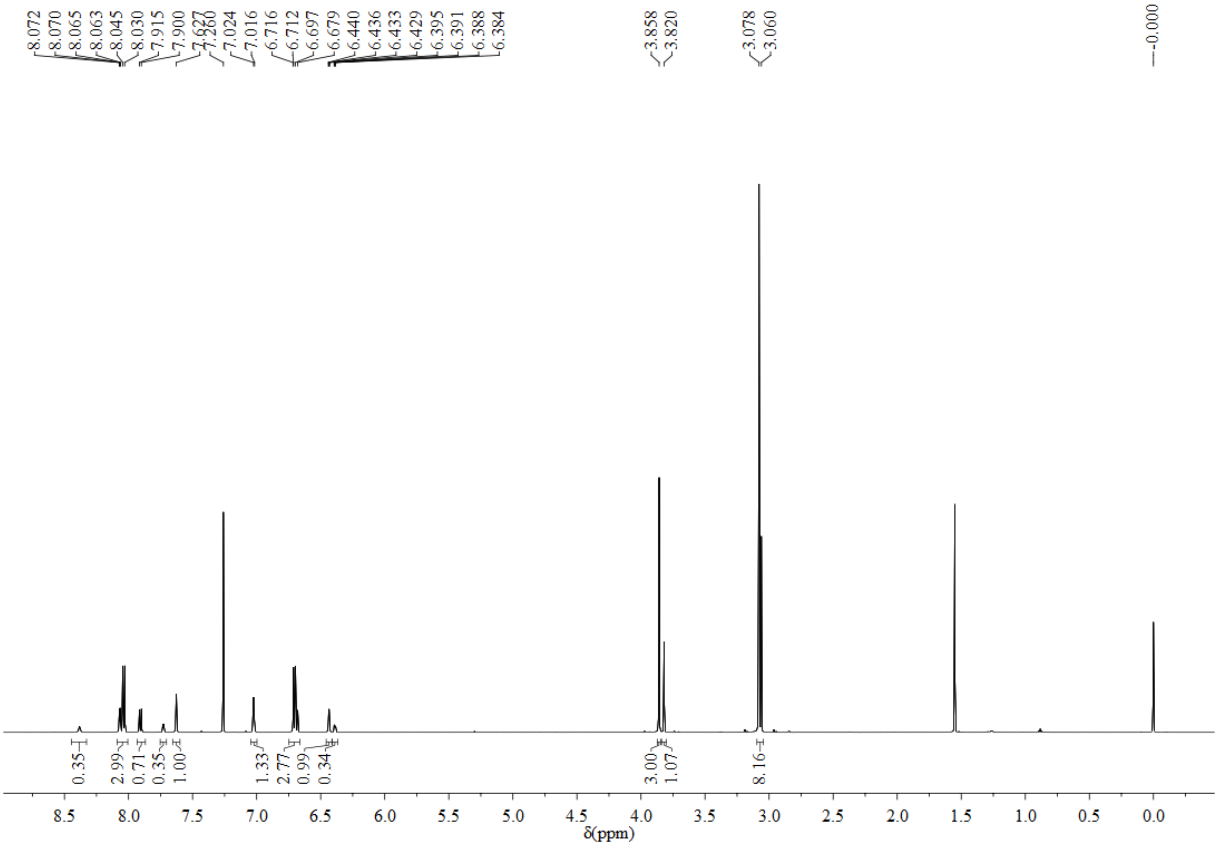
^{1}H NMR spectrum of **2a** which was irradiated by 18W white light LED for 120 min in $CDCl_3$.



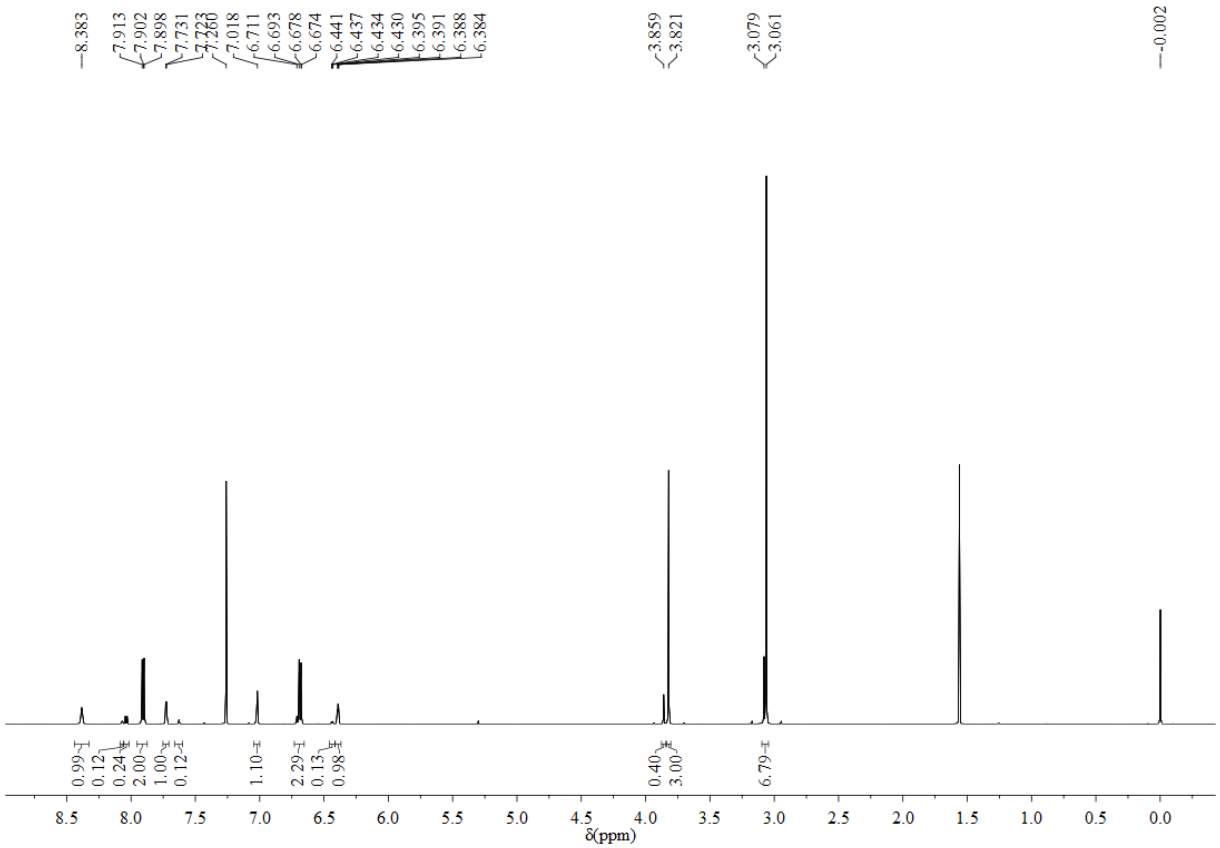
^{1}H NMR spectrum of **2a** which was irradiated by 18W white light LED for 180 min in $CDCl_3$.



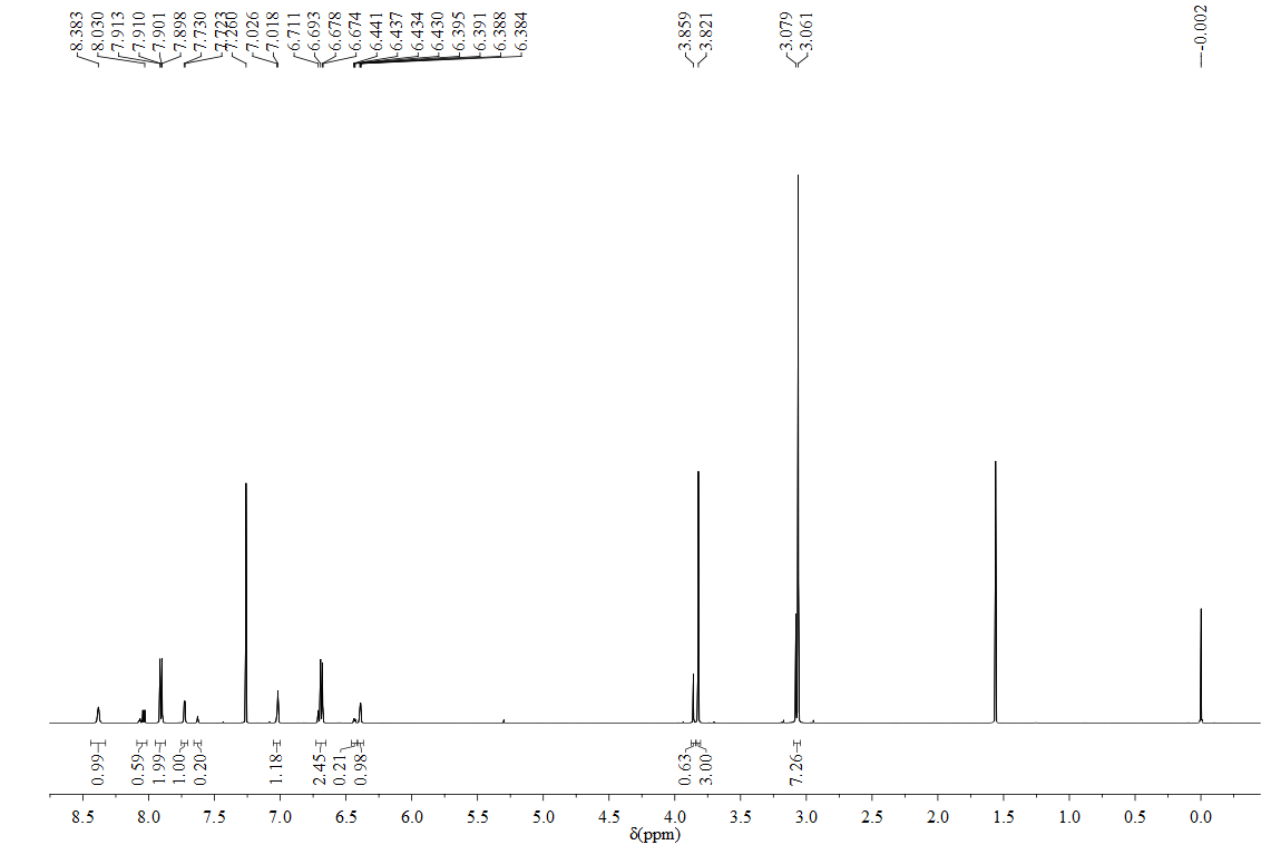
^{1}H NMR spectrum of **2a** which was irradiated by 18W white light LED for 240 min in $CDCl_3$.



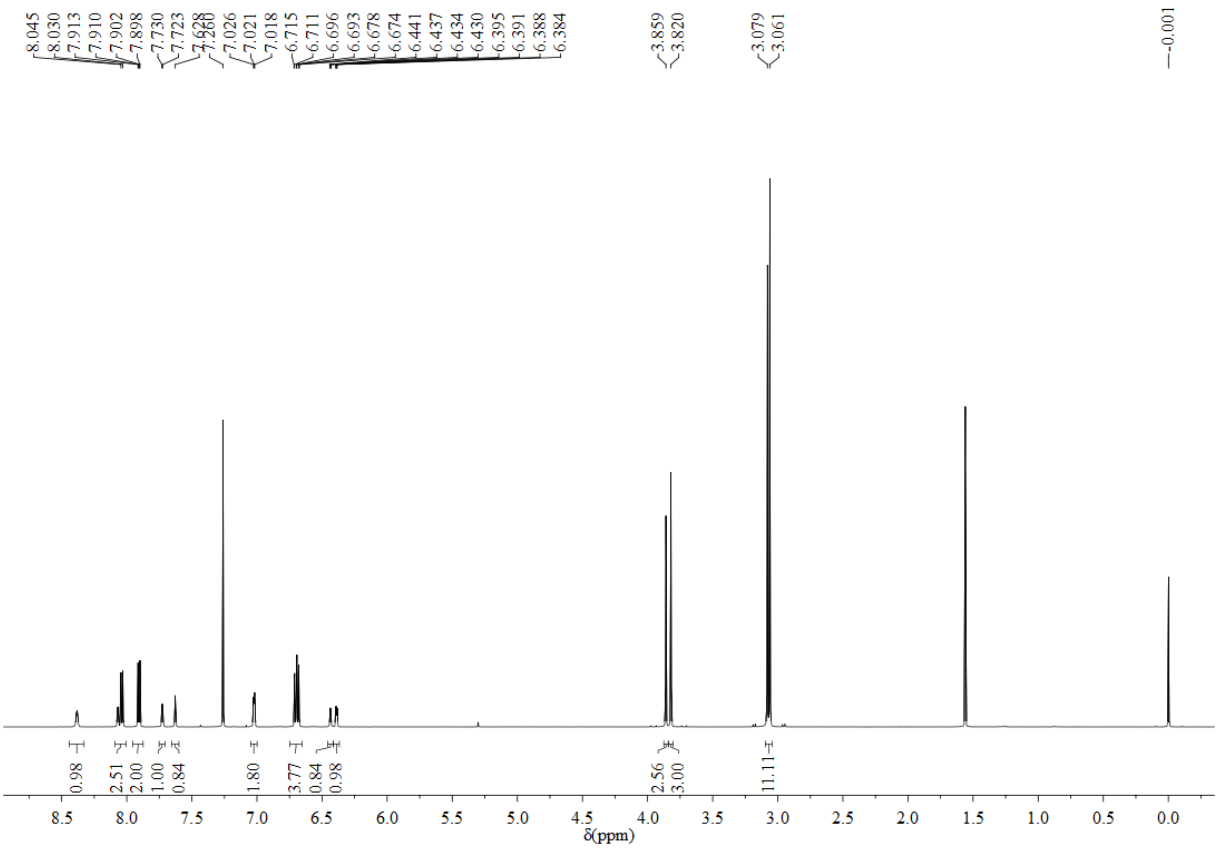
^{1}H NMR spectrum of **2a** which was irradiated by 18W white light LED for 300 min in $CDCl_3$.



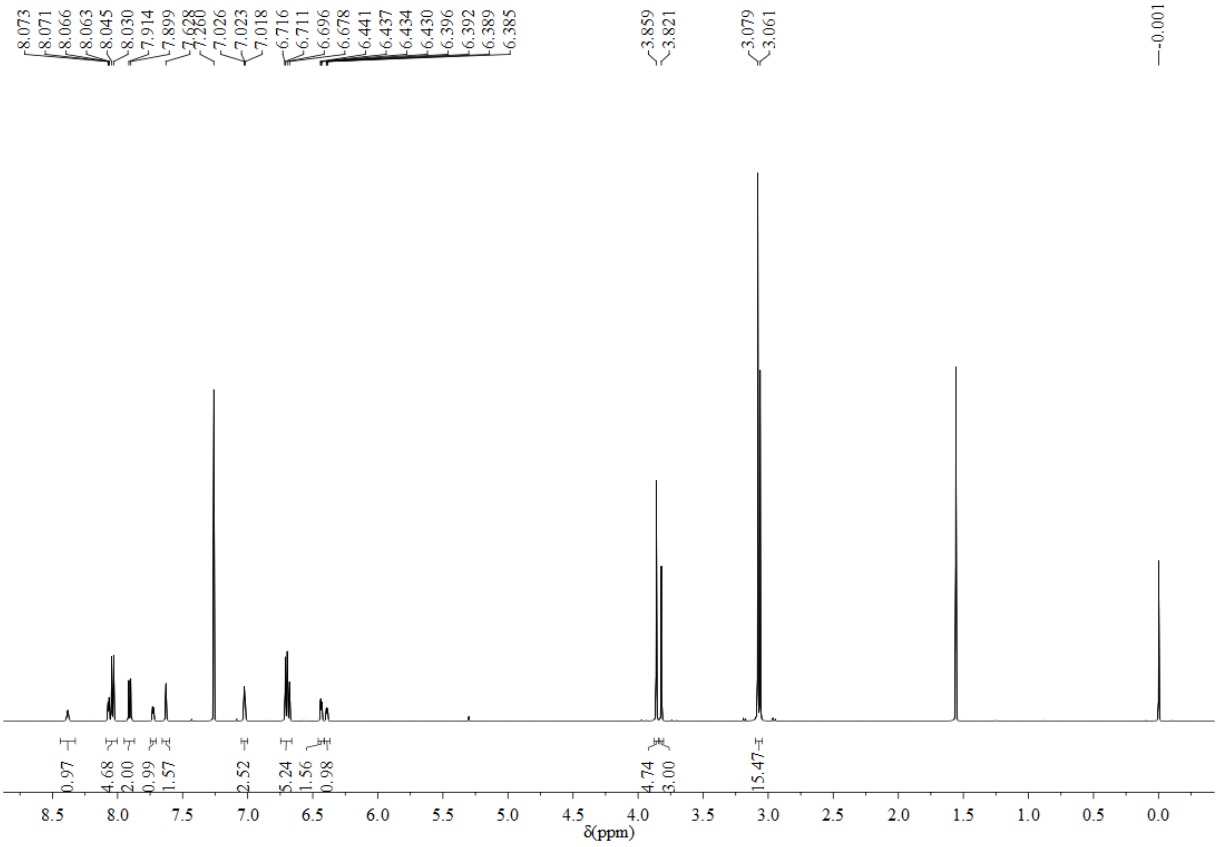
^{1}H NMR spectrum of **2b** which was irradiated by 18W white light LED for 5 min in $CDCl_3$.



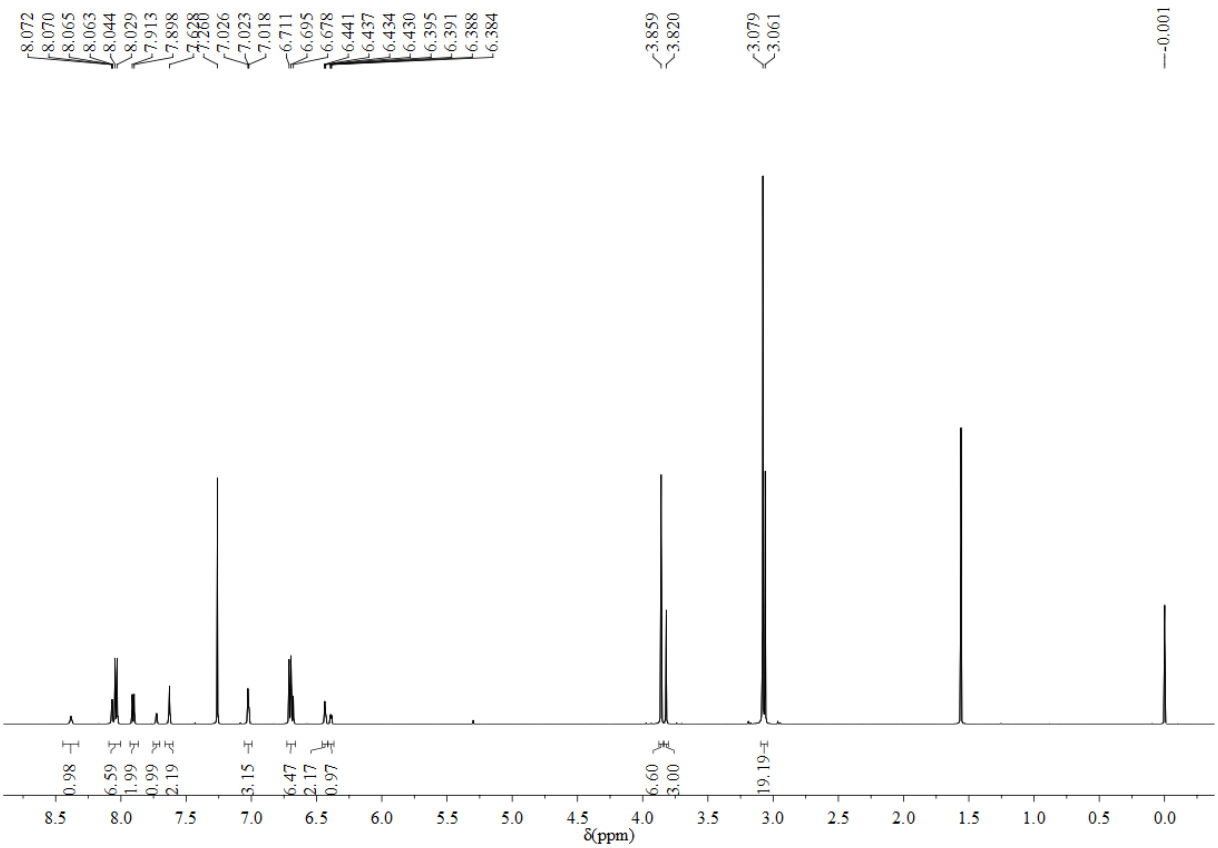
^{1}H NMR spectrum of **2b** which was irradiated by 18W white light LED for 10 min in $CDCl_3$.



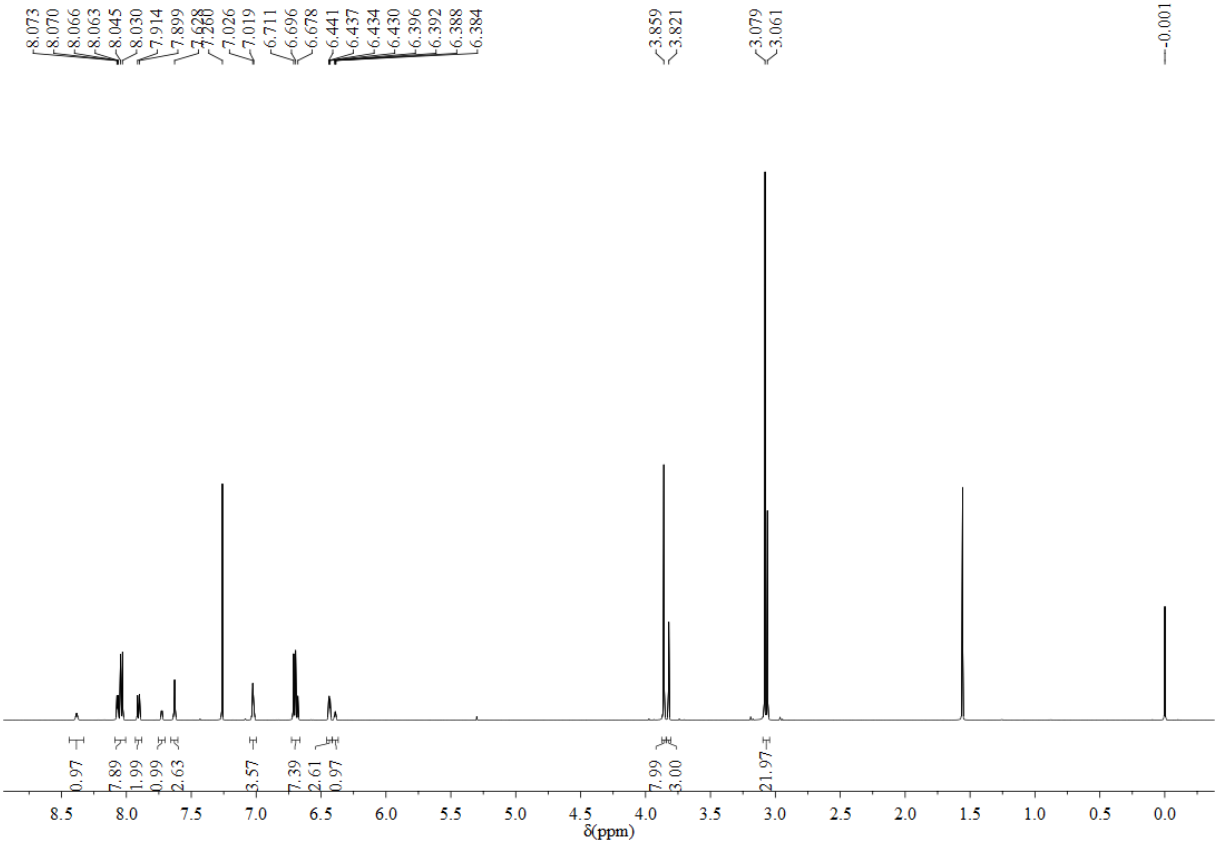
^{1}H NMR spectrum of **2b** which was irradiated by 18W white light LED for 30 min in $CDCl_3$.



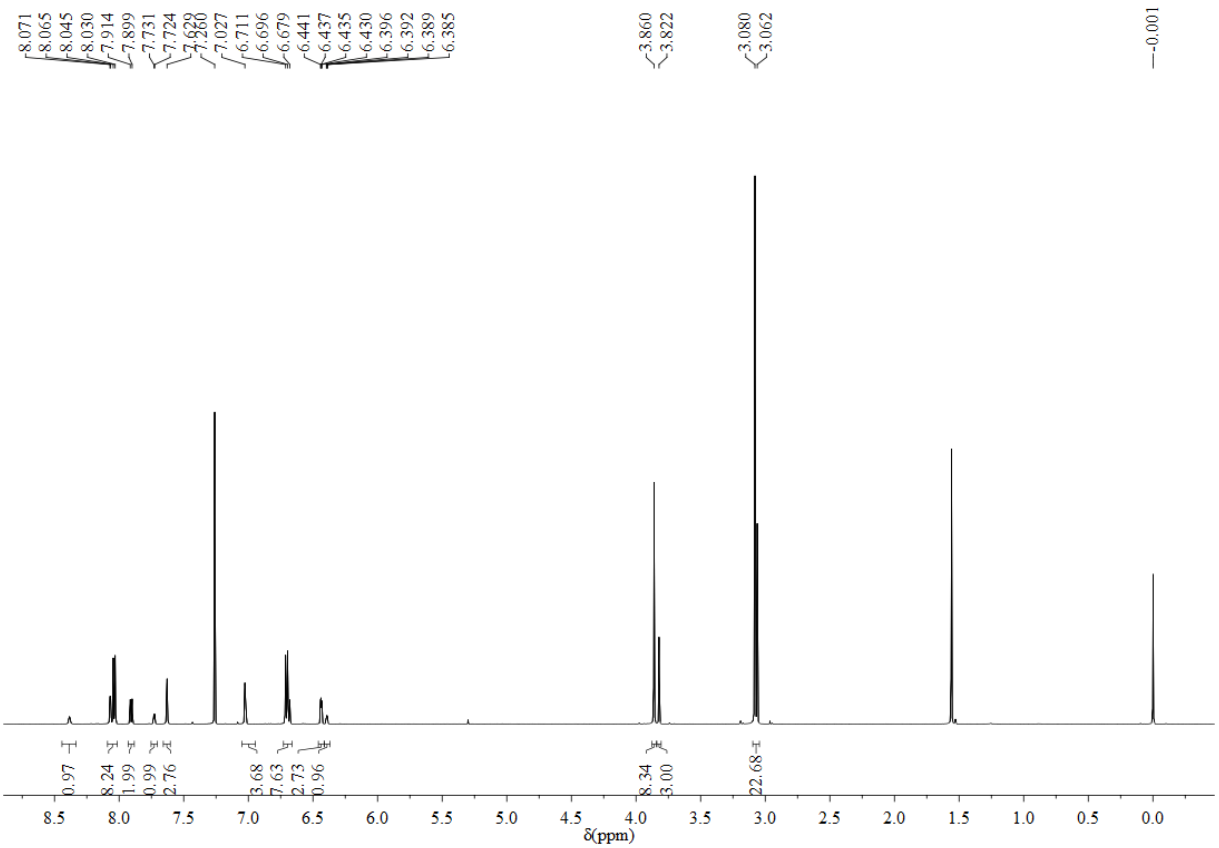
^{1}H NMR spectrum of **2b** which was irradiated by 18W white light LED for 45 min in $CDCl_3$.



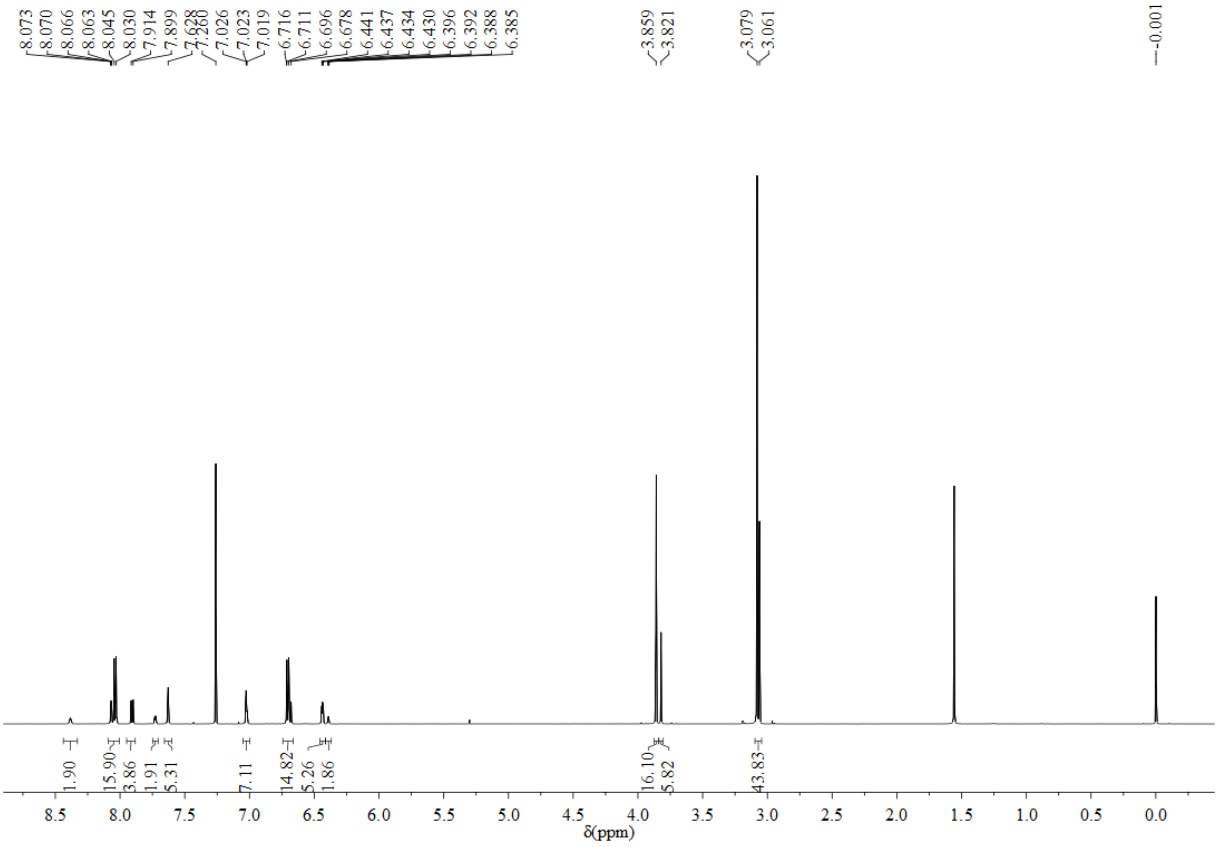
^{1}H NMR spectrum of **2b** which was irradiated by 18W white light LED for 60 min in $CDCl_3$.



^{1}H NMR spectrum of **2b** which was irradiated by 18W white light LED for 90 min in $CDCl_3$.

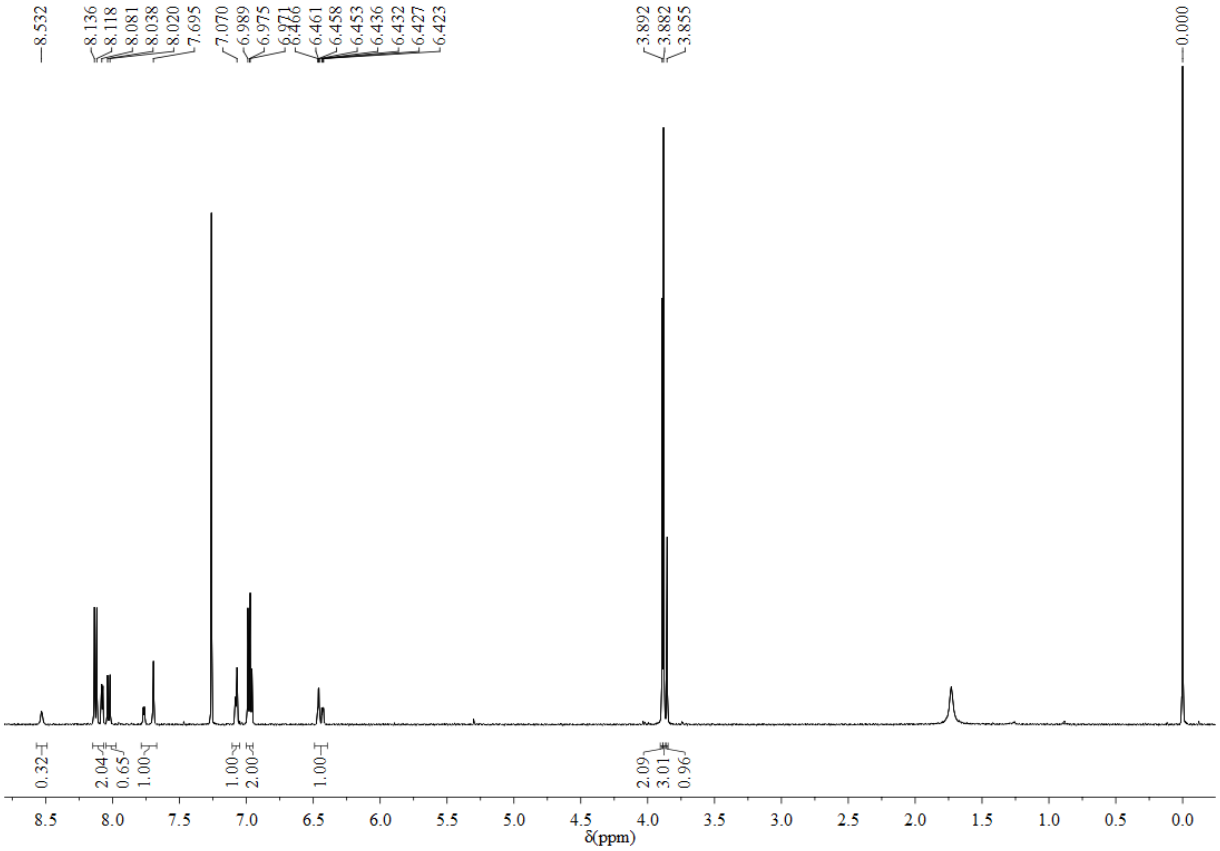


^{1}H NMR spectrum of **2b** which was irradiated by 18W white light LED for 120 min in $CDCl_3$.

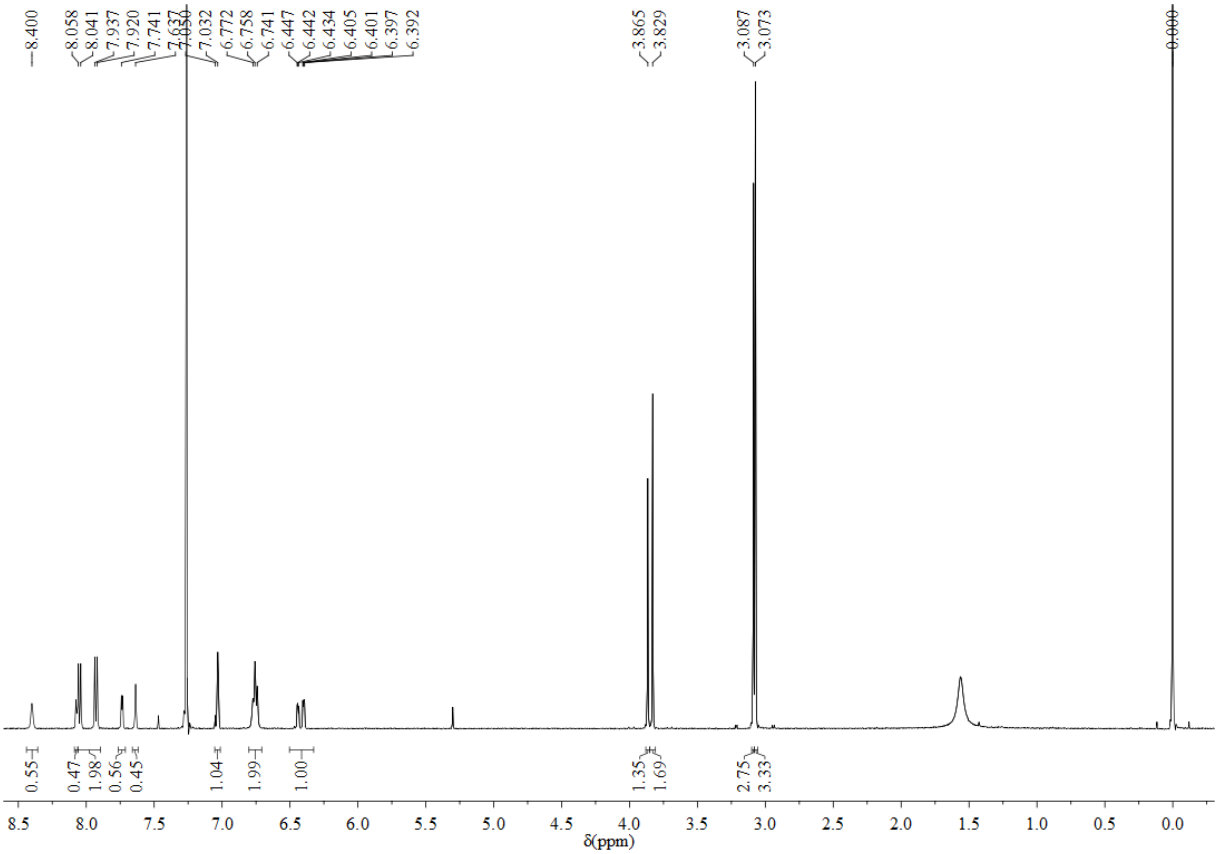


^{1}H NMR spectrum of **2b** which was irradiated by 18W white light LED for 180 min in $CDCl_3$.

6. NMR spectra for prepared isomers mixtures

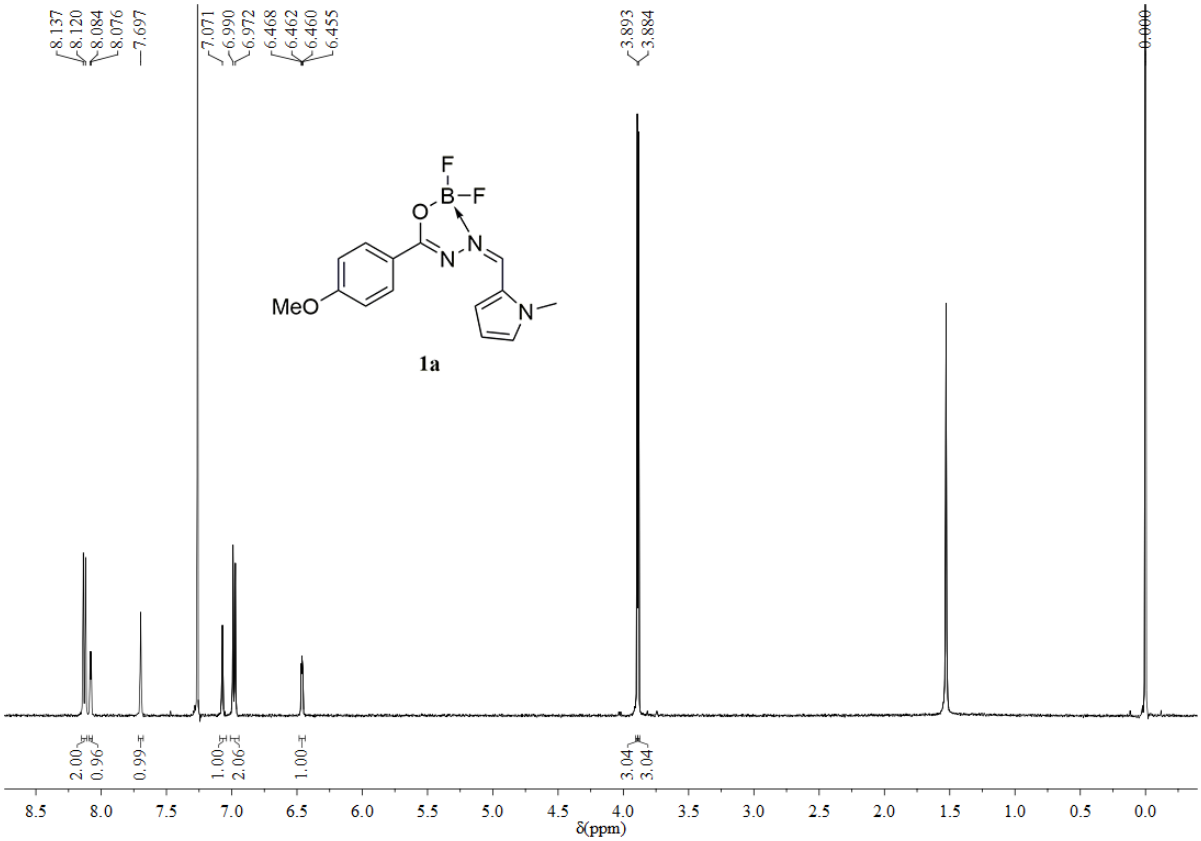


^{1}H NMR spectrum of the as-prepared crude MPOAB **1** in $CDCl_3$. The sample was obtained by column chromatography after the end of the reaction. Both isomers **1a** and **1b** were not separated/urified to demonstrate the ratio of **1a** and **1b** obtained under the reaction conditions.

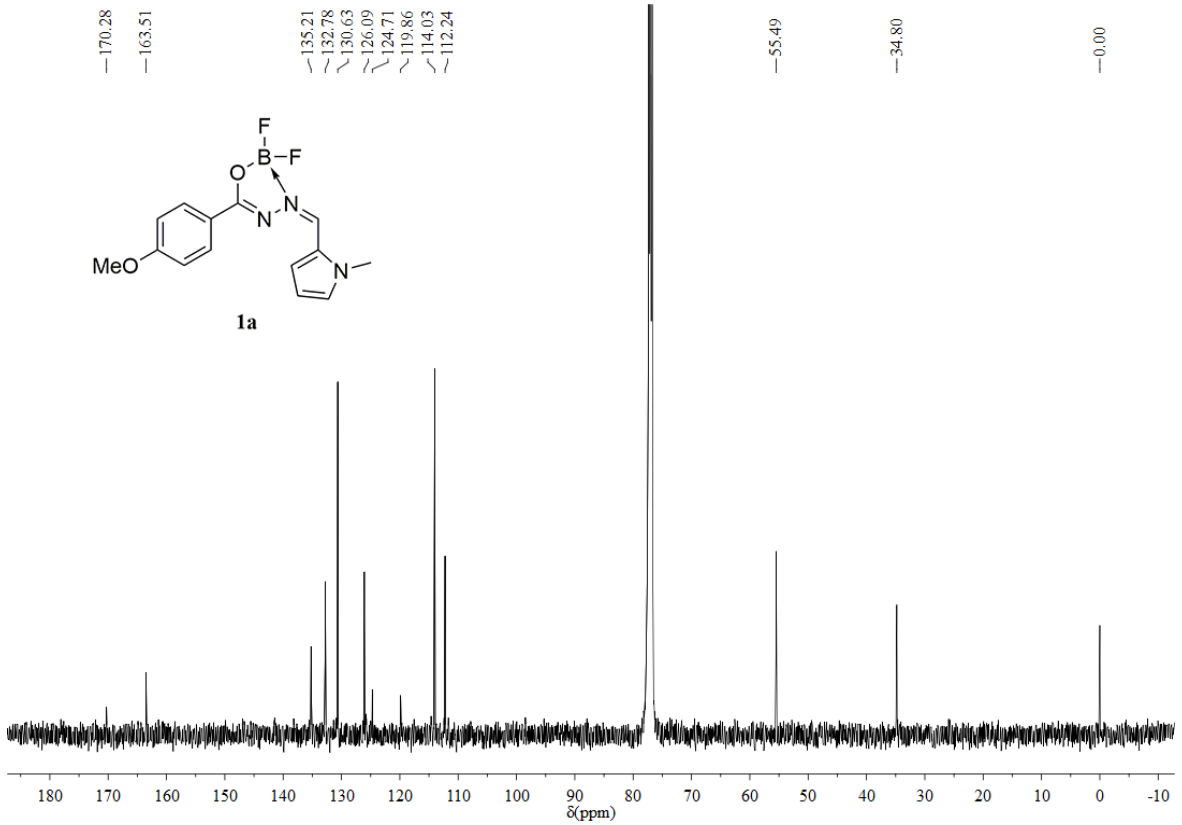


^{1}H NMR spectrum of the as-prepared crude MPOAB **2** in $CDCl_3$. The sample was obtained by column chromatography after the end of the reaction. Both isomers **2a** and **2b** were not separated/purified to demonstrate the ratio of **2a** and **2b** obtained under the reaction conditions.

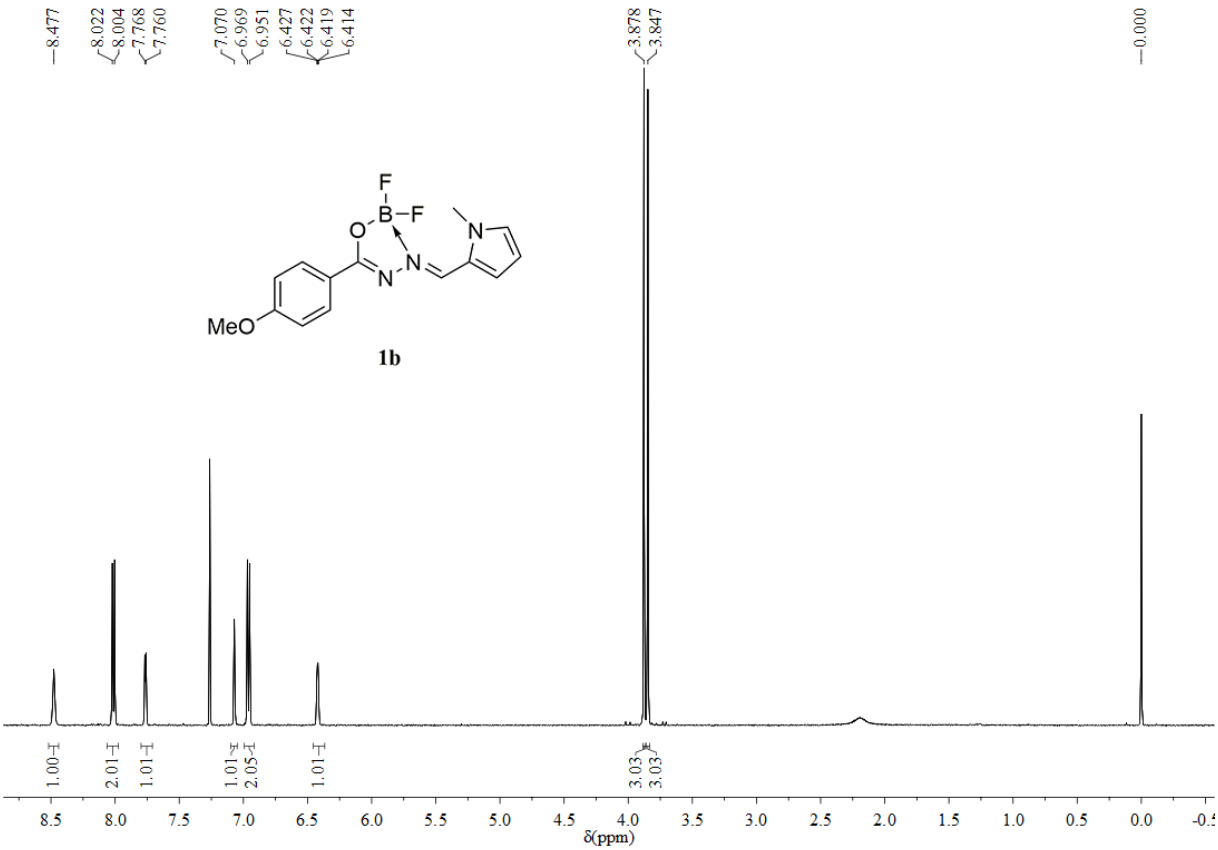
7. NMR spectra of pure isomers



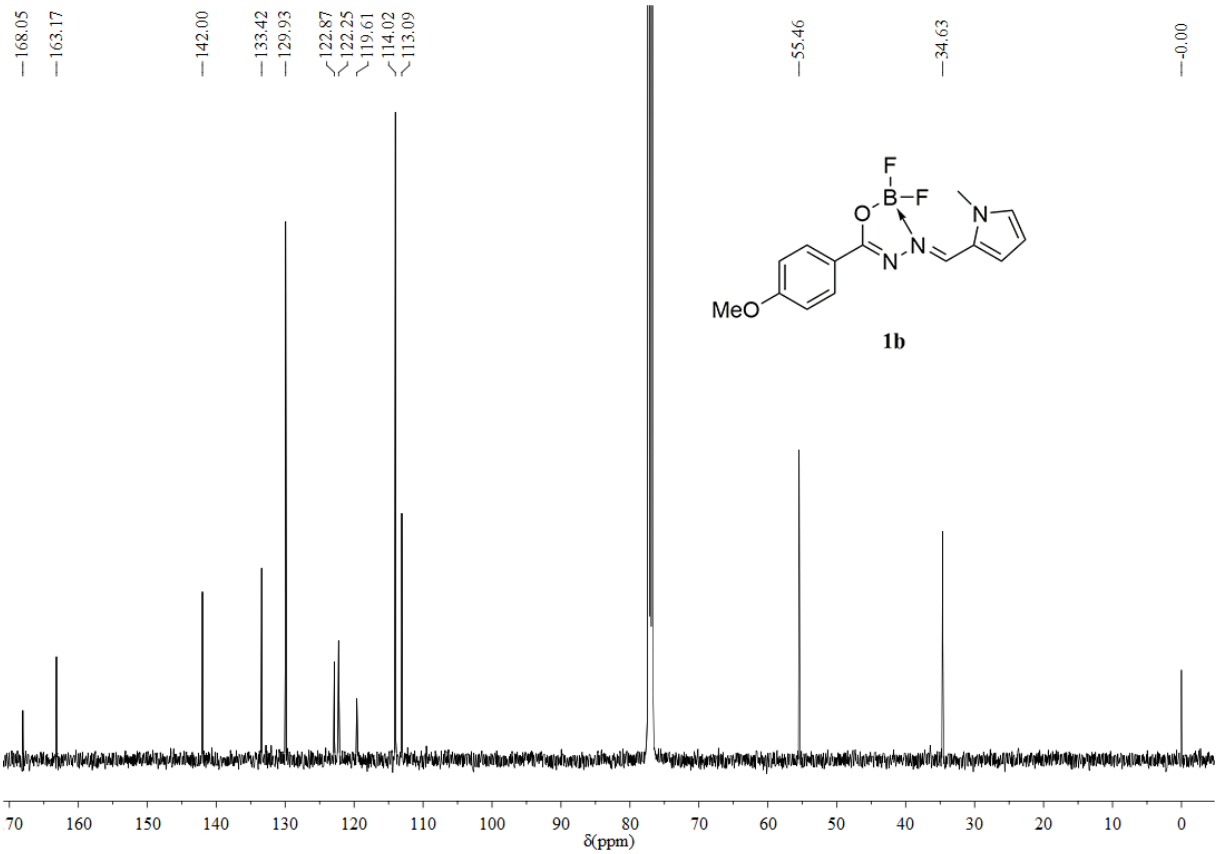
^{1}H NMR spectrum of (*Z*)-MPOAB **1a** in $CDCl_3$.



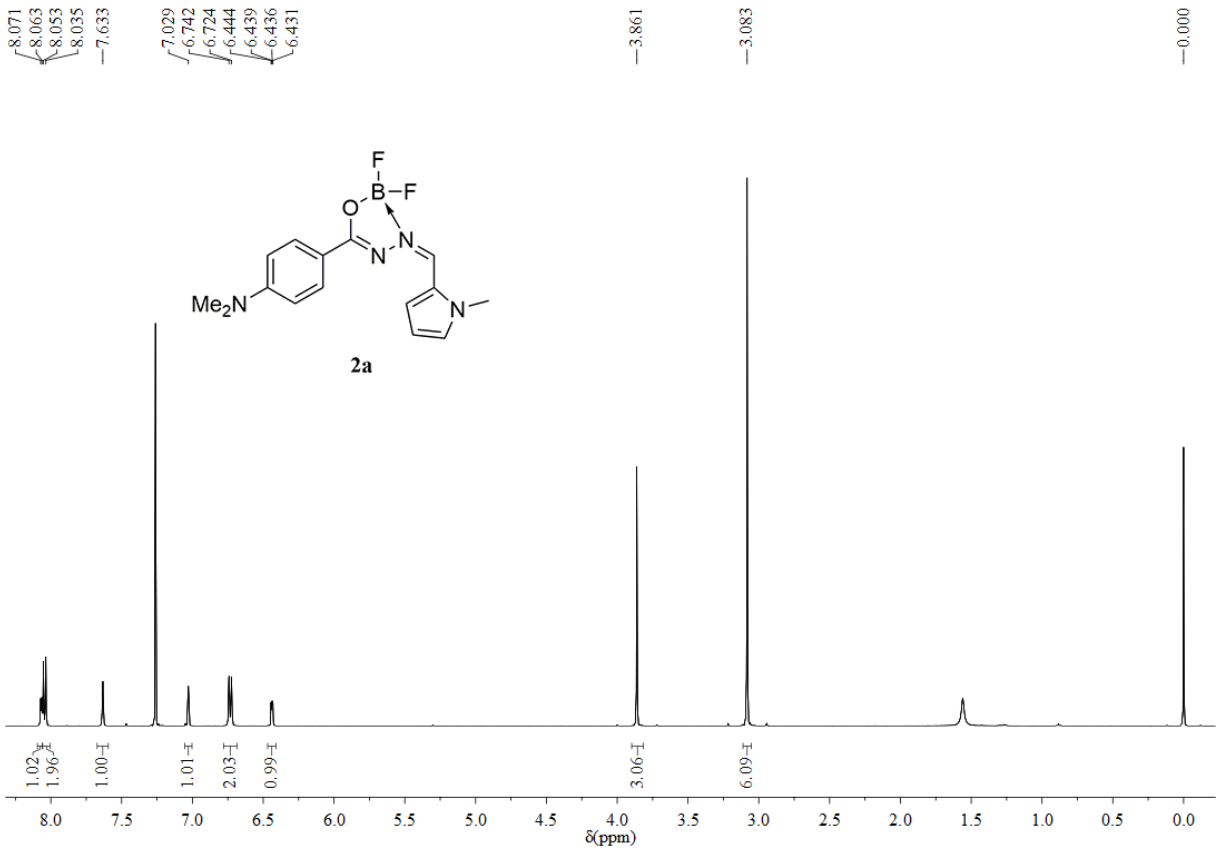
^{13}C NMR spectrum of (*Z*)-MPOAB **1a** in $CDCl_3$.



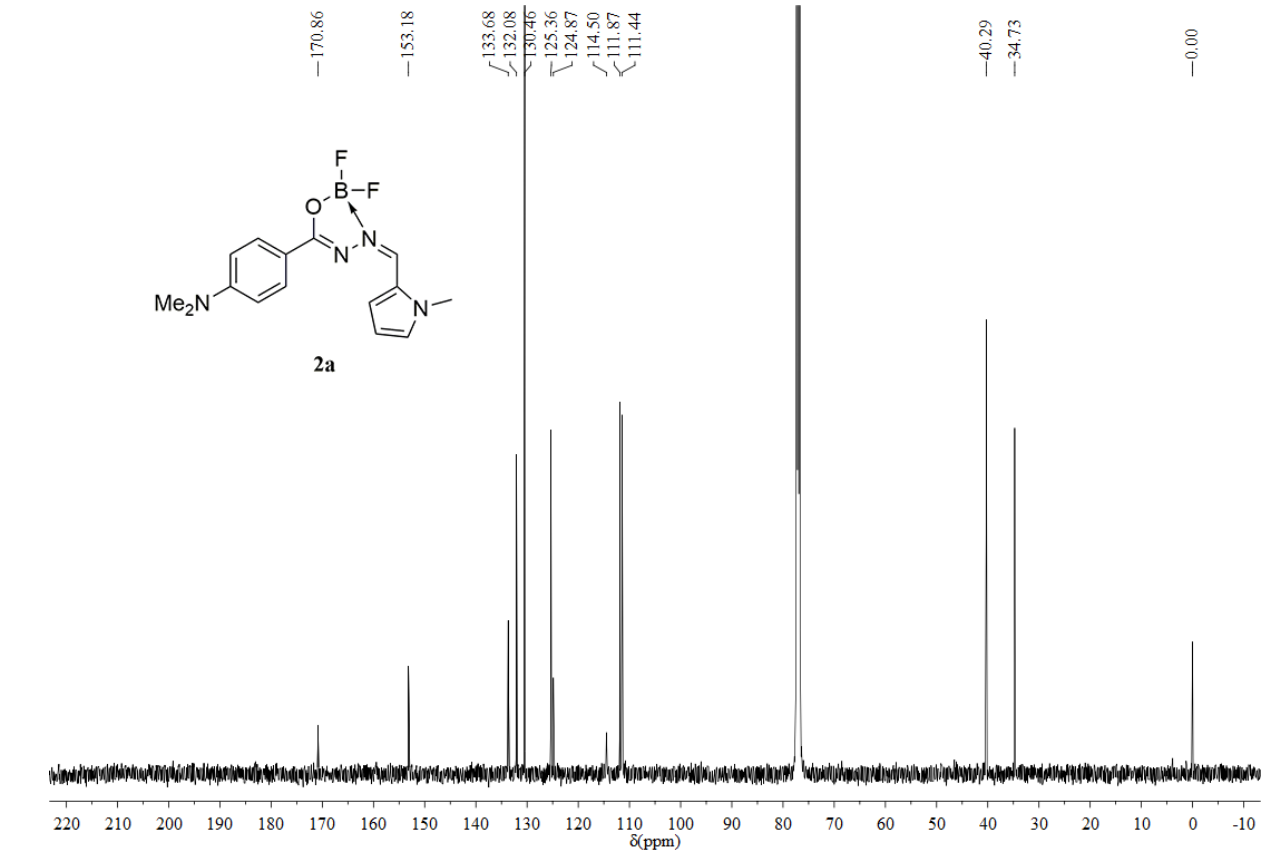
^{1}H NMR spectrum of (*E*)-MPOAB **1b** in $CDCl_3$.



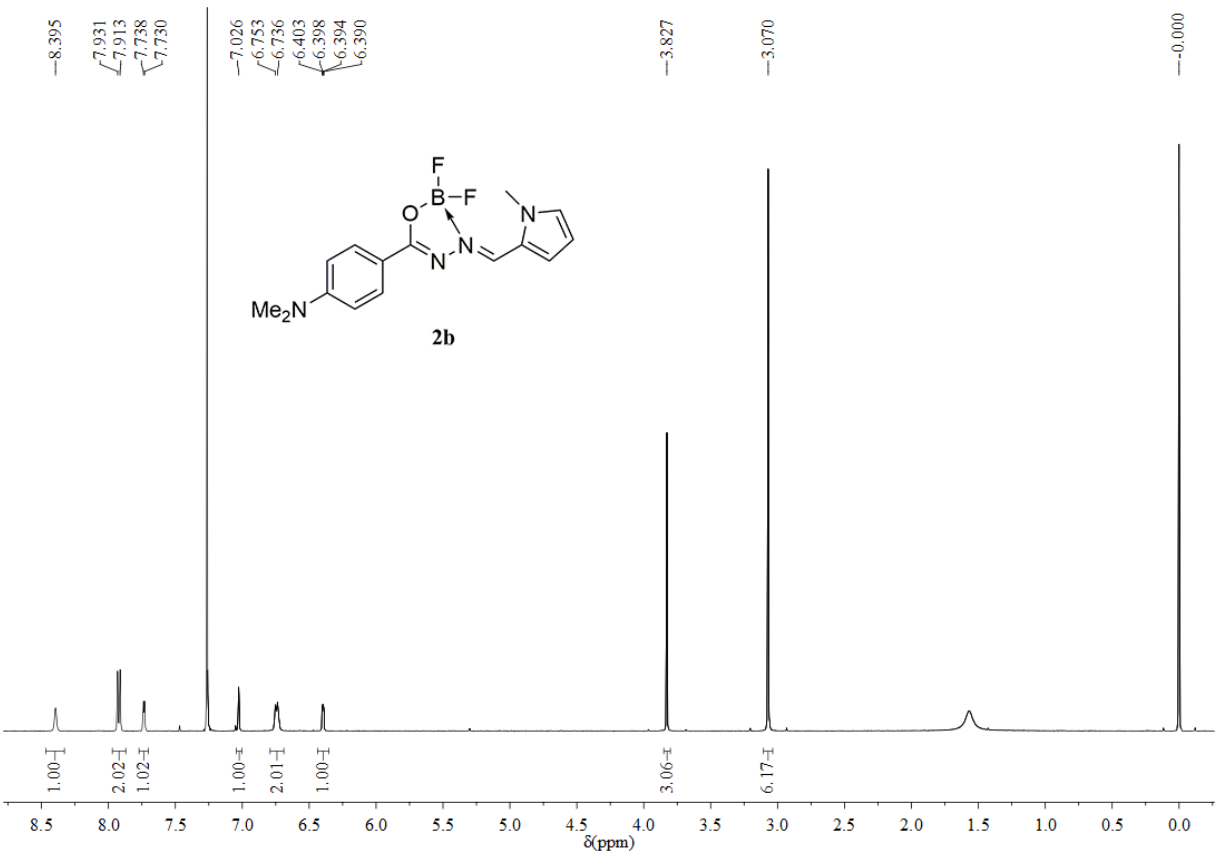
^{13}C NMR spectrum of (*E*)-MPOAB **1b** in $CDCl_3$.



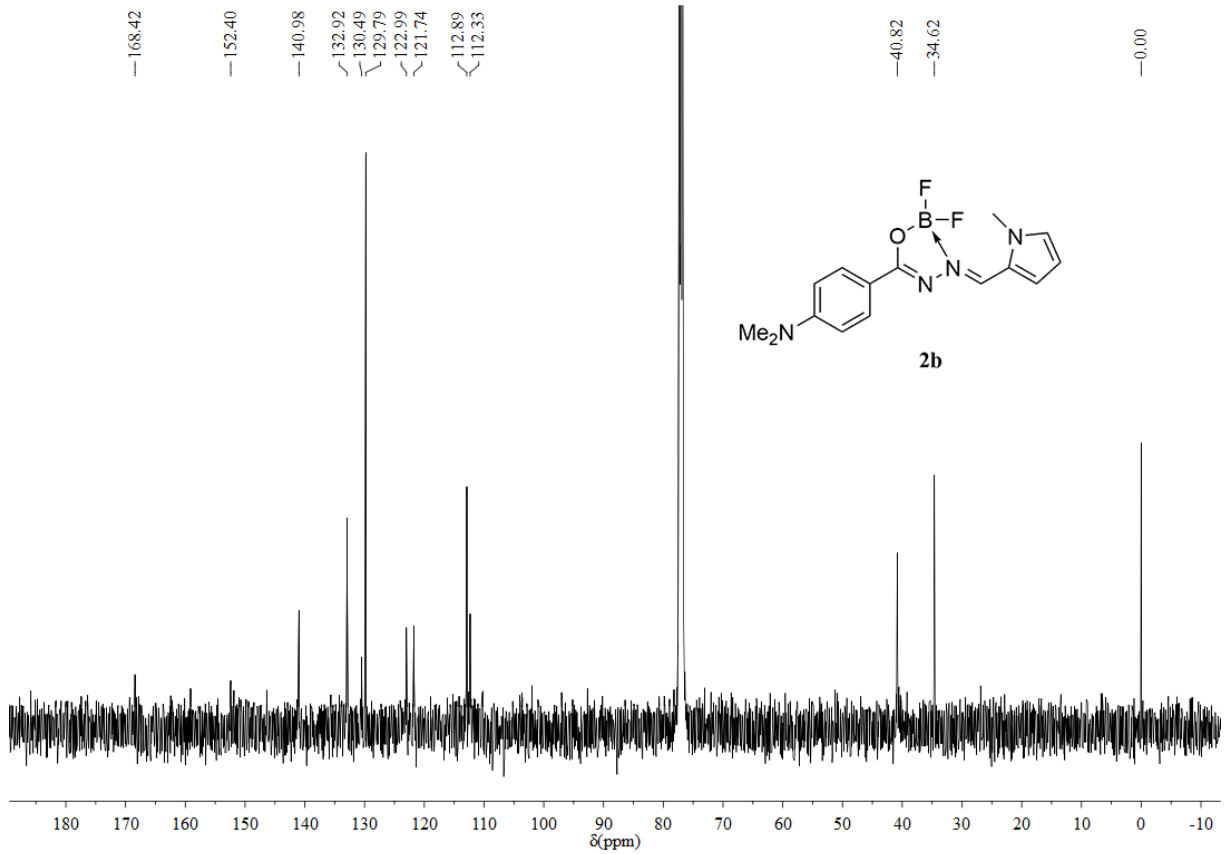
^{1}H NMR spectrum of (*Z*)-MPOAB **2a** in $CDCl_3$.



^{13}C NMR spectrum of (*Z*)-MPOAB **2a** in $CDCl_3$.



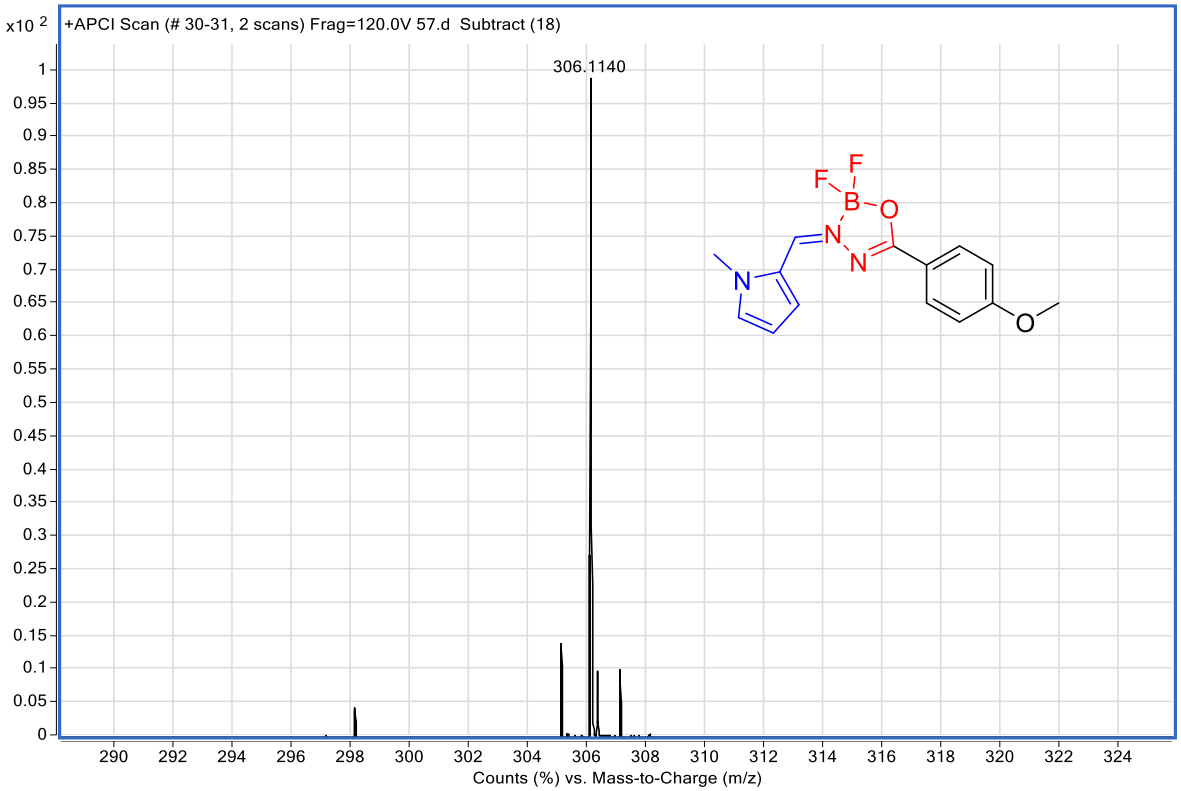
^{1}H NMR spectrum of (*E*)-MPOAB **2b** in $CDCl_3$.



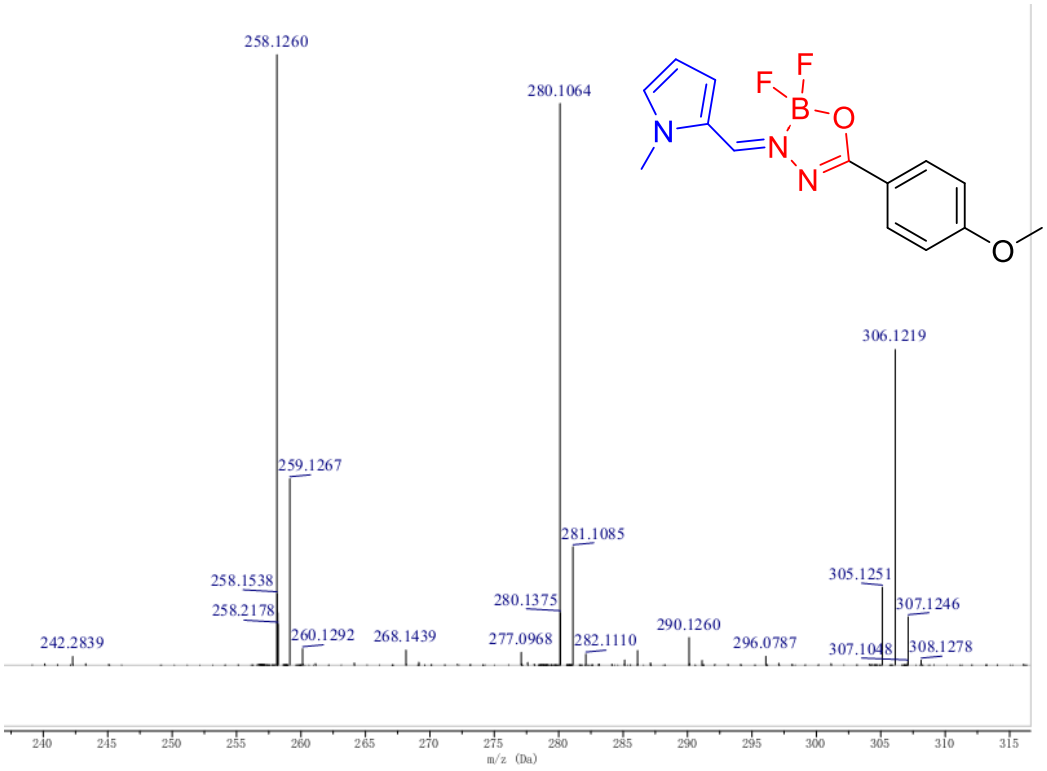
^{13}C NMR spectrum of (*E*)-MPOAB **2b** in $CDCl_3$.

8. High-resolution mass spectrum spectra

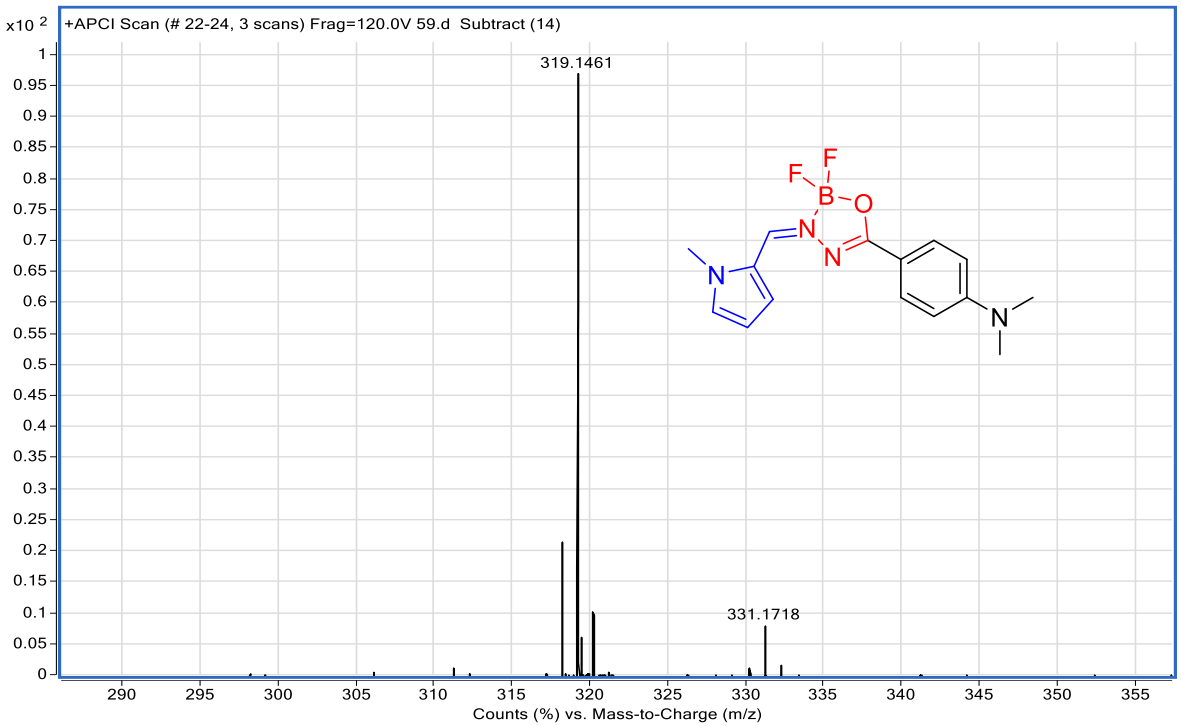
HRMS for 1a



HRMS for 1b



HRMS for 2a



HRMS for 2b